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A stochastic theory for clustering of quenched-in vacancies—IV. Continuum model applied to the formation of stacking fault tetrahedra and vacancy loops

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Abstract. The continuum model for the growth of clusters developed in the previous paper (paper III) is applied to the formation of stacking fault tetrahedra in quenched gold and the formation of faulted vacancy loops in quenched aluminium. The results of the theory namely the distribution of the clusters as a function of their size and time, and the average size and the total density of the clusters as a function of time and the ageing temperature are shown to be in good agreement with the experimental results.

Keywords. Continuum model; distribution function; stacking fault tetrahedra; vacancy loops.

1. Introduction

In the preceding papers (Ananthakrishna 1979a, b, c; referred to as papers I, II and III respectively), we have presented the various physical and mathematical reasons which lead to the development of a self-consistent continuum model which describes the growth of clusters under quenching after the initial period of nucleation. The model is applicable to cases where the number of vacancy units in the cluster is related to the linear dimension of the cluster in a quadratic way. These cases correspond to the formation of stacking fault tetrahedra and vacancy loops, both faulted and unfaulted. In this paper we shall apply the continuum model to the case of quenched gold (Jain and Siegel 1972) and quenched aluminium (Kiritani 1973). We shall first recall the two different approaches which describe the growth of clustres and make the comments which will be relevant for comparing the theoretical results with experiments.

2. The continuum model

The description of the growth of clusters can be carried out by either regarding the density of the clusters, $N(n, t)$ to be the dynamical variable of interest or by regarding the concentration of vacancies in a cluster with n vacancy units, $p(n, t)$ as the dynamical variable. In both cases we have used the asymptotic value of the concentration of single vacancy units. In the former case, after the initial nucleation period of the clusters, the total cluster density $\bar{N}Z$ is regarded as constant with a slow influx of vacancies which does not affect the value of $\bar{N}$ and contributes only to the variation

in $\langle n \rangle$. This implies that we have taken only a *near* quasi-equilibrium to have prevailed between N_1 and $N(n, t)$ in a short time during which all the clusters are formed. In this picture a strict equilibrium between N_1 and $N(n, t)$ is attained only as $t \to \infty$. In contrast, in the alternative picture, a strict equilibrium between p_1 and the rest of the clusters has been assumed to have been achieved in a short time, i.e., of the order of nucleation time. This implies that $df/dt=0$, i.e., the total number of vacancies is strictly constant throughout the growth period and only a redistribution of vacancy units among the various clusters are allowed. Equivalently we have assumed that we have introduced all the vacancy units right in the beginning. Whereas in the previous picture, $\bar{N}$ is constant and the time-dependence is entirely hidden in $\langle n \rangle$, in this picture both $\bar{N}$ and $\langle n \rangle$ are functions of time in a way which keeps the total number of vacancy units in clusters constant. These two approaches give identical results as far as the dependence on n and $\langle n \rangle$ are concerned. The difference manifests when the distribution function is considered as a function of time (or equivalently while following the total number of vacancy units in the system). Only experiments can decide which of the two approaches is relevant for a particular situation as it is possible to decide in the case of gold (Jain and Siegel 1972). The equations describing the growth of clusters in these two approaches are

$$\frac{\partial N}{\partial t} = A \frac{\partial}{\partial n} (nN) + Bn \frac{\partial^2 N}{\partial n^2} + B \frac{\partial N}{\partial n}, \tag{1}$$

and

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

The method of obtaining the solution of (1) is given in Appendix A. The method of obtaining the solution of (2) is similar to that of (1) and has already been given in Appendix B of paper III, except for inverting the solution obtained in the inverse space. The method of inverting (III. B.8) and (III. A.6) along with inverting (IV. A.6) are also given in Appendix B. Although we have given the solution of (1) and (2) in paper III, for completeness we have given the solution below. The solutions are

$$N(n, t) = \bar{K} l \exp [-l(n+\phi)] I_0 (\sqrt{n\phi}\, l). \tag{3}$$

and

$$p(n, t) = \frac{N_0^2 ln}{(N_0+x_2)\sqrt{n\phi}} \exp [-l(n+\phi)] I_1 (\sqrt{n\phi}\, l), \tag{4}$$

where

$$l = \frac{x_2}{(N_0+x_2)(1-\phi)}$$

and $\bar{K}$ is a normalisation constant to be determined. The integration constant in (3) can only be fixed as $t \to \infty$. This corresponds to the fact that a strict equilibrium between N_1 and $N(n, t)$ is obtained as $t \to \infty$. However, the change in the value of $\bar{N}$ from small times (where only a near quasi-equilibrium has been attained) to large times is very small as has been shown earlier (see the discussion following (III. 16) in

Ananthakrishna 1979c). We can fix this constants as $t\to\infty$ and compare it with (4). It is clear that as $t\to\infty$

$$\lim_{t\to\infty} N(n, t) \to \bar{K} \frac{x_2}{(N_0+x_2)} \exp\left(-\frac{x_2 n}{N_0+x_2}\right). \tag{5}$$

Using (5) in the definition of $f(t)$

$$f(\infty) = \int n\, dn\, N(n, t) = N_0^2/(N_0+x_2),$$

we get $$\tilde{K} = N_0^2 x_2^2/(N_0+x_2). \tag{6}$$

Using this in (5) we get

$$N(n, t) = \frac{N_0^2 x_2^2}{(N_0+x_2)^3} \exp\left[-\frac{x_2 n}{N_0+x_2}\right]. \tag{7}$$

It is clear that the normalisation in both cases is exactly the same as $t\to\infty$. However, the total number of vacancies changes gradually in the picture when $\bar{N}$ is kept constant. At the start of the growth of the clusters the number of vacancy units is of the order of

$$N_0 - 2N_0\, x_2/(N_0+x_2).$$

(The factor of two arises due to the time-dependent part in $N_1(t)$ at the point where the decoupling is effected, is taken to be of the same order as $N_0x_2/(N_0+x_2)$ see discussion following (III. 16).) The difference in the normalisation constant between the start and the end of the growth process, is the fraction of the vacancies that falls from the value $N_1 \sim 2N_0x_2/(N_0+x_2)$ to strictly the asymptotic value of N_1 namely, $N_0x_2/(N_0+x_2)$. This difference is clearly small and therefore as far as the normalisation is concerned, we assume that the asymptotic value of N_1 has been attained right at the start of the growth process and thus the normalisation constant for all practical purposes can be taken to be that given by (7) for all times during the growth process. The only situation where this can affect is when we consider the distribution function as a function of time. Even in this situation the difference is not likely to be detectable. The true time evolution in many systems is probably midway between the evolution given by (4) and (3), since in an actual physical situation neither $\bar{N}$ nor $f(t)$ can be expected to be constant. The experimental distribution can in some cases distinguish the two approaches as it happens in the case of gold (Jain and Siegel 1972). Thus the mathematical representation of the physical situation via $\bar{N}$ constant or $f(t)$ constant can only be carried out if one has a knowledge of the coupling that *actually* exists between the evolution of the clusters and the single vacancy units. Fortunately this coupling is very weak in the case considered and therefore the representation via (3) and (4) yield consistent results as far $\langle n\rangle$ as a function of time is concerned.

3. Calculation of averages

As far as comparison with experiments is concerned, for a major part of what we consider here, we shall use (3) with (6). Since experiments are done in the space where the linear dimension of the clusters is measured, we will have to rewrite (3) in terms of the radius of the vacancy loop r, or the edge length l, of the tetrahedra. We shall confine our attention to the formation of stacking fault tetrahedra in quenched gold (Jain and Siegel 1972) and the formation faulted vacancy loops in quenched aluminium (Kiritani 1973). We use the relation $n=\alpha\xi^2/a^2$ where α is a geometrical factor ($\alpha=1$ for stacking fault tetrahedra and $\alpha=4\pi/\sqrt{3}$ for vacancy loops) and ξ is the linear dimension of the extended defect, to convert n to ξ. It is also sufficient to consider the leading term in (3) since the next higher order contribution contains the factor $\phi x_2^2/(N_0+x_2)^2$. Then the distribution reads

$$\tilde{N}_L(\xi, t) = \frac{2\alpha N_0^2 x_2^2 \xi}{a^2(1-\phi)\,(N_0+x_2)^3} \exp\left[-\frac{\alpha x_2\,\xi^2}{a^2(1-\phi)\,(N_0+x_2)}\right], \tag{8}$$

and

$$\phi\,(t) = \exp -\frac{x_1 x_2^2 t}{N_0+x_2}. \tag{9}$$

Here we have suppressed the factor

$$\exp\left[-\frac{x_2\phi}{(1-\phi)\,(N_0+x_2)}\right]$$

since this term is almost unity for all times of practical interest. The calculation of averages can now be carried out. Using (8) we get

$$\langle n\rangle_t = \alpha\langle \xi^2/a^2\rangle_t = \frac{N_0+x_2}{x_2}(1-\phi), \tag{10}$$

the subscript t on the average indicates the time dependence. The maximum of the distribution in the ξ-space occurs at

$$\xi/a\sqrt{\alpha} = \left[\frac{(N_0+x_2)}{2x_2}(1-\phi)\right]^{1/2}.$$

Thus

$$(\xi/a)_{\max} = \frac{1}{\sqrt{2}}\,\langle \xi^2/a^2\rangle_t^{1/2}. \tag{11}$$

The total density of the clusters is given by

$$N^* = Z\,\bar{N} \simeq Z\,\bar{N}_L^T = Z\int N_L\,(\xi, t)\,d\xi = \frac{N_0^2 x_2\,Z}{(N_0+x_2)^2} \simeq x_2 Z \tag{12}$$

The value of average ξ^2 would be the same if we use the alternate approach. Using the leading part of the distribution $N(n, t)$ obtained from (4) we see that the total density is

$$N^* = \bar{N}(t)\, Z = \frac{N_0^2\, x_2}{(N_0+x_2)^2}\, \frac{Z}{(1-\phi)}.$$

Since $$\int p(n, t)\, dn = N_0^2/(N_0+x_2),$$

we see that $\langle n\rangle_t = \dfrac{N_0+x_2}{x_2}(1-\phi)$

which is identical with that calculated via the first approach.

4. Comparison with experiments

Several quantities of experimental interest can be calculated from the distribution function. The distribution function is a function of both time and temperature, and so are the averages. The results that should be compared with experiments are: (a) the shape of the distribution as a function of the size of the clusters and time, (b) the total density of the clusters as a function of temperature, (c) the average size of the clusters as a function of time and temperature and (d) the characteristic time for the growth of the clusters. The other major result that emerges is the decay of the concentration of the single vacancy units and hence some indirect information about the nucleation time which we have already discussed in detail in our earlier paper. (Ananthakrishna 1978b, paper II). We shall discuss these results one by one.

We shall first take up the case of the formation of stacking fault tetrahedra in quenched gold (Jain and Siegel 1972). It is clear from (8) that the distribution function is entirely determined by the value x_2, since all the other quantities are known. *In turn the value of x_2 is entirely determined by the average size given by* (10) *or by the total density of the clusters given by* (12). *Thus this quantity x_2 should be regarded as a parameter to be determined from experiments through the relation* (10) *or* (12). *Given the value* of $\langle L^2/a^2\rangle$ from experiments, every other quantity of interest could be determined. In the case of the formation of stacking fault tetrahedra both the experimental and the theoretical distributions are asymmetric. However, the asymmetry in the theoretical distribution is somewhat more pronounced. Using the value of $\langle L^2\rangle^{1/2} = 408$ Å and the concentration of quenched-in vacancies $N_0 = 3\times10^{-4}$, in (10), we get a value of $x_2 = 3\times10^{-8}$. This leads to the value of

$$Z\, N_L^T \left(L_{\max}^T\right) = 3{\cdot}7\times10^{12} \text{ per cm}^{-3}$$

which can be compared with the experimental value

$$N_S^E \left(L_{\max}^E\right) = 8\times10^{12} \text{ per cm}^{-3}.$$

The position of the maximum of the theoretical distribution occurs at L=290 Å. The experimental distribution has its maximum at 380 Å. This difference is due to the fact that the theoretical distribution starts from the origin whereas the experimental distribution starts from 110 Å. The total density of the clusters theoretically computed is

$$Z N_S^T = 1{\cdot}76 \times 10^{15} \text{ per cm}^{-3}$$

and the experimental value is

$$Z N_S^E = 2 \times 10^{15} \text{ per cm}^{-3}.$$

Thus we find that the agreement with the experiment is good. The plot of the distribution is shown in figure 1.

We shall now consider the time evolution of the distribution and the average size of the clusters. It is clear from (8) that as the clusters evolve, the distribution which sharply peaked for small t, evolves into a broad peak as $t \to \infty$. Also the average size increases as a function of time as is clear from (10). These two results are qualitatively in agreement with experiments. It is in connection with the time development of the clusters that one can say whether the growth of clusters is given by (3) or (4). In the case of gold, under the experimental conditions used by Jain and Siegel (1972), $\bar{N}$ remains constant during the time over which the evolution of the clusters was studied. Thus the time development is governed by the distribution given by (3). We have already determined the value of x_2 by using $\langle L^2 \rangle$ as $t \to \infty$. The values of the input parameters are the same as in table 2 of paper II except for the value of the attempt frequency which we have taken to be ten times more* than the value quoted

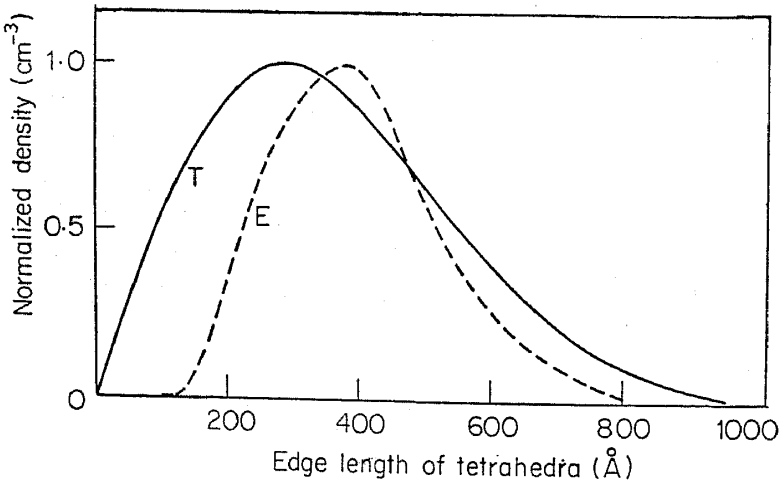

Figure 1. Normalised density of stacking fault tetrahedra as a function of the edge length. The curve T corresponds to theory and E to experiment (Jain and Siegel 1972).

*This value of ν has been arrived at by demanding that the concentration of the vacancies stored in the clusters as a function of t has nearly the same value of $t_{1/2}$, which is the time at which the concentration of vacancies in the clusters is half of that at $t = \infty$. There is a possibility that this value ν is somewhat high and may be due to the fact that the time development of clusters is a sensitive function x_2 being the square of x_1. So a small error in x_2 can affect the time development of the clusters.

in paper II (Ananthakrishna 1978b). The time evolution of the clusters has been shown in figure 2. For the sake of comparison we have plotted experimental distribution for $t=52$ min. The qualitative resemblance is quite clear. Even quantitative comparison is quite good. The peak height at $t=52$ min., in the case of theory is 1·9 times the hight at $t=\infty$. This is in good agreement with the factor of two for the corresponding quantity in the experiment. For the same case, we have calculated $\langle L^2\rangle_t^{\frac{1}{2}}$ as a function of time. A plot of $\langle L^2\rangle_t^{\frac{1}{2}}$ as a function of t is shown in figure 3. It is clear that the theoretical curve closely follows the experimental curve.

Another feature that can be considered is the temperature dependence of the total density and the average size. From (10) and (12), it is clear that their dependence on the ageing temperature are opposite, so that if the total density of the clusters falls as a function of temperature, the average size increases. This result is in agreement with experiments. Quantitative comparison can be made if either the average size or the total density of the clusters is given, since one of them would determine the value of x_2 as a function of temperature. We shall compare our theory with the

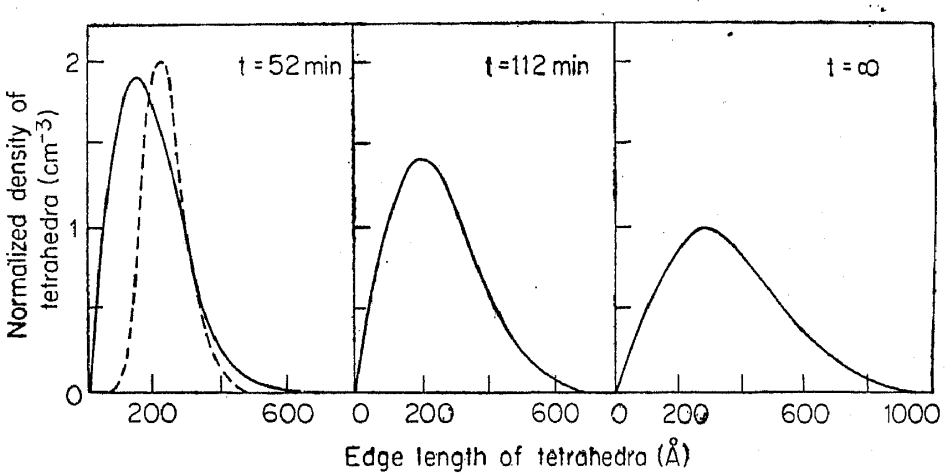

Figure 2. Time evolution of the distribution of stacking fault tetrahedra for $t=52$ min, 112 min and $t=\infty$. The density that has been normalised to the value at $t=\infty$. The curve T corresponds to theory and E to experiment (Jain and Siegel 1972).

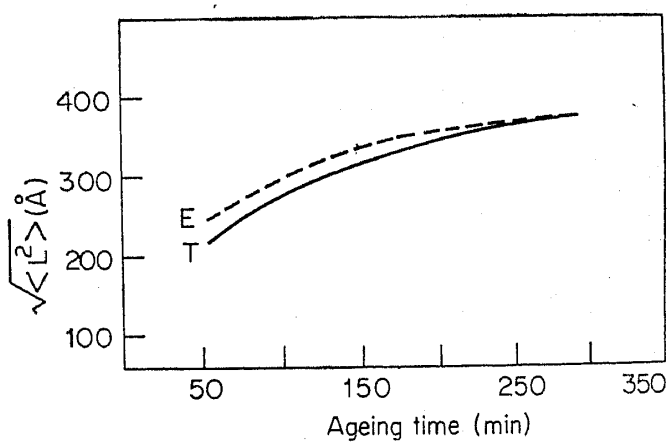

Figure 3. Time evolution of the average size of stacking fault tetrahedra at a function of time. The curve T corresponds to theory and E to experiment (Jain and Siegel 1972).

data given by Kiritani (1973) for the case of quenched aluminium. In this particular case the number of quenched-in vacancies has been estimated by using the relation

$$N_0 = \frac{4\pi}{\sqrt{3}} \langle r^2/a^2 \rangle^E N_S^E Z^{-1}, \tag{13}$$

where r is the radius of the loop. (Using the values of $\langle r^2 \rangle^E$ and N_S^E quoted in the paper, we find that the concentration of quenched-in vacancies stored in the vacancy loops is different at different temperatures in the range $T_A = -20°C$ to $30°C$. This is at variance with the value of N_0 quoted in the paper.) Using the experimental value of $\langle r^2 \rangle^{\frac{1}{2}}$ for various values of the ageing temperature, we have calculated the total density of the vacancy loops, as a function of the ageing temperature. The temperature dependence of the total density of the vacancy loops as a function is shown in figure 4. The agreement between the experiment and theory is seen to be good.

5. Discussion and conclusions

In this series of papers, we have developed a theory of clustering which has been shown to give results which are qualitatively and quantitatively in good agreement with experimental results. The basic idea is to be able to develop a model which gives a closed form expression for the distribution of clusters. This involves two aspects of the problem. The first part involves the formation of small clusters which can be called the nucleation period. The second is the growth of clusters. The first problem is somewhat tough in the sense that if the exact size distribution is to be obtained at any instant of time, it would depend on the binding energy of the cluster and thus closed form expressions are difficult to obtain (in our framework). On the other

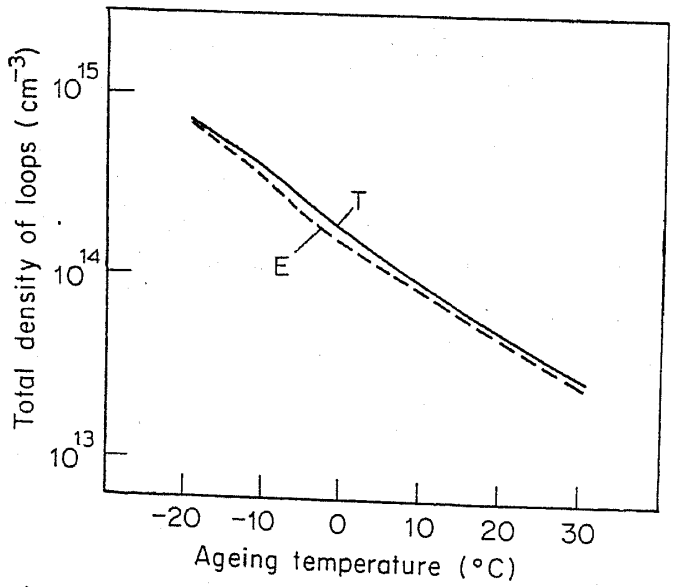

Figure 4. Temperature dependence of the total density of the faulted vacancy loops as a function of ageing temperature. The curve T corresponds to theory and E to the experiment (Kiritani 1973).

hand, the growth, problem is simpler in the sense, after the initial incubation period, which includes the nucleation period, the growth of the clusters is expected to proceed smoothly and the dependence on the binding is very minimal (Jain and Siegel 1972). Thus if in some way, information about how many clusters are formed or how much is the concentration of vacancies stored in clusters at the end of nucleation period, can be obtained the growth problem should be simpler. The idea we have pursued is to treat the first problem in a way which gives only just sufficient information to attack the growth problem. This has been done by assuming the binding to be constant even for the first part of the problem. Obviously the information obtained cannot be expected to give a correct description of the process of nucleation; yet it appears that a comparison with Kiritani computer calculation shows that our nucleation time obtained is only slightly lower than his result. This indicates that although our purpose is not one of calculation of the nucleation time, it gives confidence about the time scale and the asymptotic value for the decay of the concentration of single vacancy units which are sufficient to consider the problem of growth of clusters. In our formalism, these two are necessary ingredients that allow us to tackle the problem of growth. Indeed, it is this information that allows us to decouple the equation for the growth from the equation for the decay of N_1. However, the distribution that we obtain in the discrete model is rather unphysical and is probably due to the assumption about the constant binding energy, and improper choice of the absorption and the emission sites. This difficulty is overcome by going over into a continuum model by imposing an appropriate physically required behaviour of the distribution for small n. The resulting continuum model is also self-consistent yielding results which are in good agreement with experiments.

One important remark that we would like to make is about x_2. This quantity, now regarded as a parameter to be determined from experiment corrects for many idealisation at least partially. For instance, it is known that the impurity content of the specimen enhances the density of the clusters. *Although our theory does not include the existence of impurities and their effect on the total density of the clusters or their average size, these have been included indirectly through the parameter* x_2. This is clear because, x_2 is determined either by the total experimental density or the experimental value of the average size. Since the other quantities of interest depend on x_2, they also depend on the impurity content in the specimen indirectly. Also this parameter possibly corrects for the non-inclusion of the next mobile species which may contribute to the growth of cluster at late stages of growth.

The method of constructing continuum models for the formation of voids can be carried out along the same line with obvious complications. Also it is possible to apply the methodology to calculate the effect of impurities except for the lack of one crucial information about the ' enhancement ' factor for the density as a function of the concentration of the impurities, which would help in determining the approximate value of the range of interaction of the impurity atom with the vacancy. The method can also be applied to the formation of interstitial loops, vacancy loops and voids during irradiation. Work in these directions are being attempted.

Appendix A

Let $$\zeta(s,t) = \int_0^\infty N(n,t) \exp(-sn)\, dn. \tag{A.1}$$

Using the boundary condition on $N(n, t)$ namely

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

$$\lim_{n\to 0} nN(n, t)\to 0, \quad N(0, t) = 0 \tag{A.2}$$

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

in (1) we get

$$\frac{\partial \zeta}{\partial t} = -As\frac{\partial \zeta}{\partial s} - Bs\zeta(s, t) - Bs^2\frac{\partial \zeta}{\partial s}. \tag{A.3}$$

The characteristic solutions are

$$\frac{\zeta}{(A/B)+s}\exp(-At) = K_1 = \phi(t)\frac{\zeta}{(A/B)+s}, \tag{A.4}$$

and $$\zeta[(A/B)+s] = K_2. \tag{A.5}$$

Going through the usual algebra of eliminating K_1 and K_2 and using the usual boundary condition we get

$$\zeta(s, t) = \frac{A\exp\left[-(A/B)\dfrac{A\phi}{(A/B)+s(1-\phi)}\right]}{B[(A/B)+s(1-\phi)]}. \tag{A.6}$$

Appendix B

In this Appendix, we outline the method of inverting formulae of the type given by (A.6), (III. B.8) and (III. A.6). All these three can be written in the form

$$\lambda(s, t) = \exp\left\{-d\frac{s\phi}{[d+s(1-\phi)]}\right\}\frac{d^{\nu}}{[d+s(1-\phi)]}\mu + 1. \tag{B.1}$$

The inverse transform is given by

$$Q(n, t) = \frac{1}{2\pi i}\oint_c \exp(sn)\,\lambda(s, t)\,ds. \tag{B.2}$$

Consider writing the integrand in an appropriate manner. Setting

$$d/(1-\phi) = l \quad \text{and} \quad l + s = Z.$$

We can write

$$\frac{s}{l+s} = 1 - \frac{l}{l+s} = 1 - \frac{l}{Z}.$$

Then $$Q(n, t) = \frac{d^\nu}{2\pi i\,(1-\phi)^{\mu+1}} \oint \frac{\exp\{n(Z-1) - l\phi[1-(l/Z)]\}}{Z^{\mu+1}}\, dZ$$

or $$Q(n, t) = \frac{d^\nu \exp(-n\phi - l\phi)}{(1-\phi)^{\mu+1}\, 2\pi i} \oint \frac{\exp[nZ + (l^2\phi/Z)]}{Z^{\mu+1}}\, dZ, \tag{B.3}$$

where we could have taken the integrand over an appropriate contour since the integrand satisfies the necessary conditions (McLachlan 1963).

Equation (B.3) is of the form of the integral representation of I_μ.

$$I_\mu(t/2) = \frac{(\frac{1}{2}t)^\mu}{2\pi i} \oint \frac{\exp[Z + (t^2/4Z)]}{Z^{\mu+1}}\, dZ, \tag{B.4}$$

with the series expansions

$$I_\mu(t/2) = \sum_{m=0} \frac{(\frac{1}{2}t)^{\mu+2m}}{m!\,\Gamma(\mu+m+1)}. \tag{B.5}$$

Using this and the exact form of (A.6), (III. A.6) and (III. B.8) we obtain the corresponding expressions for $N(n, t)$ given by equations (3), (III. 7) and (4) for $p(n, t)$

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