STOCHASTIC DEVELOPMENT
OF
DISSOLUTION MORPHOLOGY

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by

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A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Engineering

McMaster University

September 1970

MASTER OF ENGINEERING — McMASTER UNIVERSITY

(Metallurgical Engineering) — Hamilton, Ontario.

TITLE: Stochastic Development of Dissolution Morphology

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NUMBER OF PAGES: (ix), 30

SCOPE AND CONTENTS:

In order to investigate the formation of different types of pit shapes on the crystalline surfaces, a mathematical model has been considered, which does not take into account surface diffusion and which defines the removal or transformation of different characteristic sites on the surface according to a set of frequencies. The characteristic sites are defined according to Terrace-Ledge-Kink model for the simple cubic crystal. With the help of the geometry of the step systems, specific conditions have been obtained under which the step systems considered could be obtained for a pit of monoatomic thickness. The dissolution of a simple cubic crystal has been simulated according to a set of probabilities.

ACKNOWLEDGEMENT

The author wishes to acknowledge the help of the supervisor, Dr. M. B. Ives, for his numerous suggestions and interest in the research problem.

Thanks are also due to Dr. R. Kelly and Dr. M. L. Tiku for stimulating discussions on certain aspects of the problem.

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LIST OF SYMBOLS

a_j the number of jth characteristic site at time t = 0

A total number of sites on the surface.

C_j designation for the jth characteristic site

d_{rel} ratio of the diameter of a sphere with a volume equal to N_R times the volume occupied by an atom in the unit cell to an atom diameter.

d_{sphere} diameter of a sphere with a volume equal to N_R times the volume occupied by an atom in the unit cell.

d_{at} atom diameter

$e(C_j)$ overall probability for removal of the jth characteristic site

e_{34} relative probability of removal of kink site with respect to that of the in ledge site

j designation for the jth characteristic site

K cumulant generating function

$\overline{K}$ ratio of the rate of change of in-ledge sites to the rate of change of kink sites

L an integer defining the number of the perfect pit, the smallest sized pit being designated as L = 1.

$m_j(t)$ mean value of the number of the jth characteristic site at time t.

M moment generating function

n_j the number of the jth characteristic site

$\bar{n}(C_j)$ the number of the jth characteristic site

N_R total number of atoms removed from the surface for a particular pit

$N(C_3)$ number of kink atoms at the perfect pit

$N(C_4)$	number of in ledge atoms at the perfect pit
p	the probability of a particular state on the surface
P	probability generating function
$P(C_j)$	instantaneous probability of removal of the jth characteristic site
γ	random number between 0 and 1
SITE(j)	number of jth characteristic site on the surface at time t
$SITE_j$	Sample mean of the jth characteristic site on the surface
$(SITE_j)$av.	Population mean of the jth characteristic site
t	time
V_u	volume of the unit cell
n_u	number of atoms in the unit cell
x_j	dummy variables
$x_j(t)$	the random variable pertaining to the jth characteristic site
θ_j	dummy variables
μ_j	frequency of removal of the jth characteristic site
λ_j	frequency of change of the jth characteristic site to (j-1)th characteristic site.

Introduction

When a close-packed crystal face is considered in contact with an etchant, dissolution of the crystal sets in since the chemical potential of the crystal substance in the etchant is lower than the chemical potential of the crystal. Dissolution takes place by step movement. The sources of steps will be screw dislocations, two dimensional nuclei of dissolution (hollows of monoatomic thickness in the surface layer of the lattice), sub-grain boundaries and the crystal edges.

The theoretical analyses of crystal dissolution that are most widely accepted today can be grouped into two categories: (a) those which invoke a mechanistic approach as first rigorously applied by Burton, Cabrera and Frank (1); (b) those based upon phenomenological or kinetic arguments such as the topographical theory of Frank (2). Both types of theories follow the concepts of Kossel (3) and Stranski (4) who developed the currently-accepted geometric model for vicinal crystalline surfaces. This model of the surface with the various characteristic sites on the surface is called TLK model. If the crystal is exemplified as a regular simple cubic lattice, the sites of which are occupied by atoms depicted as cubes, then the typical sites on the surface which may arise may be schematically illustrated as in Figure 1. Ledges and especially kink sites along the ledges are energetically preferred sites for removal of atoms from a crystalline surface. Hence, dissolution occurs by the recession of a train of monoatomic ledges across the surface (5). The localized dissolution rate will be proportional to the product of the ledge velocity (v) and the concentration of ledges (k) in the given vicinity. The theoretical analysis of the dissolution processes then involves an interpretation of the dependence of v on k. The significant

difference between the mechanistic approach and the topographical theory is that in the former, Burton, Cabrera and Frank invoked the ledge model of dissolution and derived v equal to v(k), whereas in the latter, Frank assumed a form for v(k) and then developed his theory.

In practice, the etch pits have been found to have varying shapes from conical to pyramidal. Even for the same crystalline material, different types of pit shapes are obtained on the surface depending on the process variables (6,7). The summary of the experimentally-obtained pit shapes for NaCl is shown in Figure 2 and Figure 3 along with the conditions under which they were obtained. Ives (8) tried to explain qualitatively the different pit shapes on the basis of undersaturation of the solution and the inhibitor concentration in the solution. It was postulated that kink nucleation is primarily controlled by the undersaturation of the dissolving species in the solvent and the principal effect of etchant inhibitor is in the retardation of kink motion. The present study has been made to pin-point the values of the process variables at which a transition can take place from one type of pit shape to another.

In order to study the different pit shapes, a mathematical model was considered which took into account the removal of the different characteristic sites from the surface and the transformation of a particular characteristic site into another characteristic site according to a set of frequencies. The solution was obtained by considering the process as a stochastic process of birth and death type. From the solution obtained, conditions were derived in terms of the frequencies for obtaining the different pit shapes.

Also, since the processes occurring on the surface of a crystal are random in nature, computer simulation of the dissolution process was

thought to be appropriate in order to verify the conditions under which the different pit shapes are obtained. The computer simulation technique has previously been successfully used in the surfaces field by Moore (9) to study surface diffusion, by Chernov (10,11) to investigate random walk processes and kinetic order disorder transition in crystal growth and by Bertocci (12) to estimate the relative importance of random nucleation and step motion on the growth rate of crystals.

The model for computer simulation was that of a section of a crystal surface from which dissolution took place through the removal of different atomic units according to a set of parameters defined initially for each of the characteristic sites.

Mathematical Analysis

Introduction

A very simple model has been used for studying the distribution of the different characteristic sites on the surface. The model does not take into account surface diffusion. For the simple cubic crystal, there are five characteristic sites on the surface, the atoms at these sites have less than their full complement of neighbouring atoms, and these are characterized in chemical terms as having lower coordination than atoms in the interior of the crystal. According to the notation of Nicholas (13), under the assumption that only the effect of the first nearest neighbours is taken into account, a surface atom with j nearest neighbours will be said to have coordination j and will be referred to as an atom of type j or C_j. The five sites can then be defined according to Table 1.

The Model

Consider a system containing the different characteristic sites on the surface of the crystal and undergoing statistical fluctuations in the density of the different characteristic sites. Two processes which take place on the surface are postulated: (i) whenever a particular characteristic site is removed from its position on the surface (independent of the number of nearest neighbours it may have) it gives rise to an in-terrace site; (ii) Due to the effect of (i), the number of nearest neighbours of the neighbouring sites to the site removed is modified and a transition to a lower next nearest neighbour site takes place.

The process as depicted above is a multi-dimensional process, there are five phases in the present case and the frequency of the removal μ_j (j = 1,2,3 and 4) of the five characteristic sites will be different from each other as the different characteristic sites on the surface have different energies. Also, the frequency of a change of site from a particular coordination (j) to the next lower coordination (j-1) is λ_j (j = 2,3,4 and 5) and is different for different j's.

The above process is sketched in Figure 4 and the different frequencies are designated accordingly. The tail of the arrow indicates a decrease by one in the species toward which the tail is and the head indicates an increase by one in the species towards which the head is.

The stochastic development of the process will be fully described once the function

$$p\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}, t\Bigg)$$

is known, which is the probability that at time t the number of individuals of the jth characteristic sites is n_j (14). At $t = 0$, a_j ($j = 1,2,3,4$ and 5) denote the number of the characteristic sites present on the surface of the jth type. In order to derive the differential equation describing the course of fluctuations, it is necessary to consider the possible transitions, in the interval of time $(t, t + \Delta t)$ which lead from the state

$$\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}$$

into other states and the transition which bring the system from other states into

$$\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_2 \\ n_1 \end{pmatrix} .$$

The differential equation describing the process can be written if we adopt the convention that $p \equiv 0$, whenever any of the n_j are negative. It will then readily be seen that

$$\frac{\partial}{\partial t} p\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}, t = \lambda_5 (n_5+1)\, p\begin{pmatrix} n_{5+1} \\ n_{4-1} \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}, t + \lambda_4 (n_4+1)\, p\begin{pmatrix} n_5 \\ n_{4+1} \\ n_{3-1} \\ n_2 \\ n_1 \end{pmatrix}, t$$

$$+ \lambda_3 (n_3+1)\, p\begin{pmatrix} n_5 \\ n_4 \\ n_{3+1} \\ n_{2-1} \\ n_1 \end{pmatrix}, t + \lambda_2 (n_2+1)\, p\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_{2+1} \\ n_{1-1} \end{pmatrix}, t$$

$$- (\lambda_5 n_5 + \lambda_4 n_4 + \lambda_3 n_3 + \lambda_2 n_2)\, p\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}, t$$

$$+ \mu_1 (n_1+1)\, p\begin{pmatrix} n_{5-1} \\ n_4 \\ n_3 \\ n_2 \\ n_{1+1} \end{pmatrix}, t + \mu_2 (n_2+1)\, p\begin{pmatrix} n_{5-1} \\ n_4 \\ n_3 \\ n_{2+1} \\ n_1 \end{pmatrix}, t$$

$$+ \mu_3 (n_3+1)\, p\begin{pmatrix} n_{5-1} \\ n_4 \\ n_{3+1} \\ n_2 \\ n_1 \end{pmatrix}, t + \mu_4 (n_4+1)\, p\begin{pmatrix} n_{5-1} \\ n_{4+1} \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}, t$$

$$- (\mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \mu_4 n_4)\, p\begin{pmatrix} n_5 \\ n_4 \\ n_3 \\ n_2 \\ n_1 \end{pmatrix}, t \qquad (1)$$

If we introduce the generating function

$$P\begin{pmatrix} x_5 \\ x_4 \\ x_3, t \\ x_2 \\ x_1 \end{pmatrix} = \sum x_1^{n_1} x_2^{n_2} x_3^{n_3} x_4^{n_4} x_5^{n_5} \; p\begin{pmatrix} n_5 \\ n_4 \\ n_3, t \\ n_2 \\ n_1 \end{pmatrix} \quad (2)$$

it will follow that when (2) is applied to (1), (2) must satisfy the partial differential equation

$$\frac{\partial P}{\partial t} = \sum_{j=2}^{5} \lambda_j \, (x_{j-1}-x_j) \, \frac{\partial P}{\partial x_j} + \sum_{j=1}^{4} \mu_j \, (x_5-x_j) \, \frac{\partial P}{\partial x_j} \quad (3)$$

the associated boundary condition is

$$P\begin{pmatrix} x_5 \\ x_4 \\ x_3, 0 \\ x_2 \\ x_1 \end{pmatrix} = x_1^{a_1} x_2^{a_2} x_3^{a_3} x_4^{a_4} x_5^{a_5} \quad (4)$$

The final system of differential equations for the variation of mean value of the number of each characteristic site with time as obtained in Appendix I from equations (3) and (4) are

$$\frac{dm_1(t)}{dt} = -\mu_1 m_1(t) + \lambda_2 m_2(t)$$

$$\frac{dm_2(t)}{dt} = -(\lambda_2+\mu_2)\, m_2(t) + \lambda_3 m_3(t)$$

$$\frac{dm_3(t)}{dt} = -(\lambda_3+\mu_3)\, m_3(t) + \lambda_4 m_4(t)$$

$$\frac{dm_4(t)}{dt} = -(\lambda_4+\mu_4)\, m_4(t) + \lambda_5 m_5(t)$$

$$\frac{dm_5(t)}{dt} = -\lambda_5 m_5(t) + \mu_1 m_1(t) + \mu_2 m_2(t) + \mu_3 m_3(t) + \mu_4 m_4(t) \qquad (5)$$

where $m_j(t)$ designates the mean value of the number of the jth characteristic site present on the surface at time t. Up to now, it has not been possible to find the nature of the distributions for the different characteristic sites, although the different equations (5) for the mean value of each of the characteristic site have been obtained.

For the general process λ_j and μ_j are generally unknown and a straightforward solution of (5) is not possible. However, if λ_j and μ_j do not depend on time, then one can express the solution of the equations (5).

The solution of the system of equations(5) along with their initial conditions $m_j(0) = a_j$ (j = 1,2,3,4 and 5) have been obtained in Appendix II and Appendix III for two cases. In both the cases, λ_j and μ_j have been taken independent of time.

Solution for Multilayered Pit

In Appendix II, the solution for the general case was tried. The complete solution was not possible, although it can be obtained by numerical techniques. The final result would be of the form

$$m_j(t) = \sum_{i=1}^{4} c_{ij} e^{s_i t} + c_{j5} \qquad j = 1,2,3,4 \text{ and } 5 \qquad (6)$$

The constants c_{ij}, c_{j5} and s_i are not known at the present. This case is applicable when multilayered pits are obtained on the surface, in other

words, when the sources of steps are screw dislocations, subgrain boundaries, and the crystal edges.

Solution for a Pit of Monoatomic Thickness

In Appendix III complete solution was obtained for the equations (5) under the assumption

$$\sum_{j=1}^{5} m_j(t) = A = \text{constant} \qquad (7)$$

which means that the sum of all the characteristic sites on the surface is constant at any time. This is possible when the sources of steps are two-dimensional nuclei of dissolution (hollows of monoatomic thickness in the surface layer of the lattice). This is an idealized case. The final results for this case as obtained in Appendix III are:

$$m_1(t) = \frac{\lambda_2\lambda_3\lambda_4\lambda_5 A}{N}\left[1-e^{-(\mu_1+\frac{\lambda_2}{4})t}\right] + a_1 e^{-(\mu_1+\frac{\lambda_2}{4})t}$$

$$m_2(t) = \frac{\lambda_3\lambda_4\lambda_5\mu_1 A}{N}\left[1-e^{-(\lambda_2+\mu_2-\lambda_3)t}\right] + a_2 e^{-(\lambda_2+\mu_2-\lambda_3)t}$$

$$m_3(t) = \frac{\lambda_4\lambda_5(\lambda_{2+}\mu_2)\mu_1 A}{N}\left[1-e^{-(\lambda_3+\mu_3-\lambda_4)t}\right] + a_3 e^{-(\lambda_3+\mu_3-\lambda_4)t}$$

$$m_4(t) = \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)\mu_1 A}{N}\left[1-e^{-(\lambda_4+\mu_4-\lambda_5)t}\right] + a_4 e^{-(\lambda_4+\mu_4-\lambda_5)t}$$

$$m_5(t) = \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)\mu_1 A}{N}\left[1-e^{-(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)t}\right] + a_5 e^{-(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)t}$$

where $N = (\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)(\mu_1+\lambda_5) + \lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\mu_1-\mu_4)$

$$+ \lambda_4\lambda_5(\lambda_2+\mu_2)(\mu_1-\mu_3) + \lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)$$

The above equations have the same form and can be written as

$$m_j = L_j + (a_j - L_j)\, e^{-X_j t} \qquad j = 1,2,3,4 \text{ and } 5 \qquad (8)$$

where

$$L_1 = \frac{\lambda_2\lambda_3\lambda_4\lambda_5 A}{N} \qquad X_1 = \mu_1 + \frac{\lambda_2}{4}$$

$$L_2 = \frac{\lambda_3\lambda_4\lambda_5\mu_1 A}{N} \qquad X_2 = \lambda_2 + \mu_2 - \lambda_3$$

$$L_3 = \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)\mu_1 A}{N} \qquad X_3 = \lambda_3 + \mu_3 - \lambda_4$$

$$L_4 = \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)\mu_1 A}{N} \qquad X_4 = \lambda_4 + \mu_4 - \lambda_5$$

$$L_5 = \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)\mu_1 A}{N} \qquad X_5 = 4\mu_1 - \mu_2 - \mu_3 - \mu_4 + \lambda_5$$

It has been verified that irrespective of the values of λ_j and μ_j, N is always positive. Therefore L_j (j = 1,2,3,4 and 5) will always be a positive quantity.

Variation of Mean Values with Time Under Limiting Conditions

The mean value of the number of any characteristic site is dependent on the values of L_j, a_j and X_j. By giving different values to L_j, a_j and X_j, we can find how m_j will vary with time.

1. a_j and L_j both non-zero

   (a) $X_j < 0$, then from (8)

   (i) when $a_j > L_j$ at $t = 0$, $m_j = a_j$; $t \to$ large, $m_j \to$ large

   i.e. the mean value of the number of the jth characteristic site increases with time.

(ii) when $a_j < L_j$ at $t = 0$, $m_j = a_j$; $t \to$ large, $m_j \to -$(large)

i.e. the mean value of the number of the jth characteristic site decreases with time and becomes negative. When $m_j < 0$, this case does not operate as m_j can never be negative.

(iii) when $a_j = L_j$ at $t = 0$, $m_j = a_j$;; any t, $m_j = a_j$

i.e. the time average of the mean value of the number of the jth characteristic site is constant.

(b) $X_j > 0$, then from (8)

(i) when $a_j > L_j$ at $t = 0$, $m_j = a_j$; $t \to$ large, $m_j \to L_j$

i.e. the mean value of the number of the jth characteristic site reaches a limiting value L_j at large times.

(ii) when $a_j < L_j$ at $t = 0$, $m_j = a_j$; $t \to$ large, $m_j \to L_j$

i.e. same as (i).

(iii) when $a_j = L_j$ at $t = 0$, $m_j = a_j$; any t, $m_j = a_j$

i.e. time average of the mean value of the number of the jth characteristic site is constant.

(c) $X_j = 0$

Irrespective of the value of a_j and L_j, at $t = 0$, $m_j = a_j$; any t, $m_j = a_j$ i.e. the time average of the mean value of the number of the jth characteristic site is constant.

m_j has been plotted schematically against t for the above cases in Figure 5.

2. $a_j = 0$, then (8) becomes

$$m_j = L_j (1 - e^{-X_j t})$$

(i) $X_j > 0$ at $t = 0$, $m_j = 0$; $t \to$ large, $m_j \to L_j$

i.e. m_j increases with time

(ii) $X_j = 0$ at $t = 0$, $m_j = 0$; any t, $m_j = 0$

In this case, the jth characteristic site does not have a chance to increase its population.

(iii) $X_j < 0$ at $t = 0$, $m_j = 0$; $t \to$ large, $m_j \to$ negative m_j

This case is not possible, since m_j can never be negative.

The schematic plot of m_j against t has been shown in Figure 6 for these cases.

3. $L_j = 0$, then (8) becomes

$$m_j = a_j e^{-X_j t}$$

(i) $X_j = 0$ at $t = 0$, $m_j = a_j$; any t, $m_j = a_j$

i.e. the time average of the mean value of the number of the jth characteristic site is constant.

(ii) $X_j > 0$ at $t = 0$, $m_j = a_j$; $t \to$ large, $m_j \to 0$

i.e. the mean value of the number of the jth characteristic site decreases till it becomes zero in the limit.

(iii) $X_j < 0$ at $t = 0$, $m_j = a_j$; $t \to$ large, $m_j \to$ large

i.e. m_j increases with time.

The schematic plot of m_j against t has been shown in Figure 7 for these three cases.

Discussion of Kinetics of Dissolution

There are in all twelve different cases which can be applicable for the jth characteristic site. For the ad-atom and at-ledge sites (under the assumption of no surface diffusion) the energy with which these sites are bound in the surface is very small. We assume that as soon as these sites are formed, they are removed from the surface. The kinetics of dissolution of ad-atom site is then determined by the case 3(ii) and the kinetics of dissolution of at-ledge site is determined by the cases

(1(a(ii))) and (3(ii)). For the in-ledge and kink sites, the processes are complex since none of these sites tend to a zero value. There is generally a net density of kink and in-ledge sites on the surface. On this basis, we can say that kinetics of dissolution and formation of these sites are governed by all the cases considered except cases (1(a(ii))) and (3(ii)). The in-terrace sites decrease with time, but their number on the surface can never become extinct. The only case that determines the kinetics of the in-terrace sites is thus (1(b)(i))).

Depending upon what has been said above, we can say that the kink and in-ledge sites are the only ones which are important in determining the shape of the pit. Thus it is necessary to determine the ratio m_4/m_3 (which is the ratio of the mean number of in-ledge sites at any time to the mean number of kink sites at the same time) by considering the combinations of the different cases which are applicable for kink and in-ledge sites respectively.

Conditions for Pit Shapes

In order to study the conditions under which different pit shapes are formed, it is necessary first to subdivide the cases whose solution can be expressed by the equation (8). It simply means that we should subdivide the cases which fall under the general area of the pit of monoatomic thickness. There are two such cases:

(i) Perfect surface

(ii) Surface with a system of steps.

By perfect surface we mean that initially the surface consists of only the in-terrace sites and by surface with a system of steps we mean that there is already a hollow of monoatomic thickness on the surface with an initial distribution of kink and in-ledge sites.

Using equation (8), we next consider different surface conditions and find the limiting values of m_4/m_3 for them.

A. Perfect Surface

Perfect surface means at t = 0, only the in-terrace sites are present. The initial surface conditions are then $a_1 = 0$, $a_2 = 0$, $a_3 = 0$, $a_4 = 0$ and $a_5 = A$. Nucleation of a two-dimensional hole is necessary for the dissolution to take place. From (8), for the initial conditions, we obtain

$$m_j = L_j (1-e^{-X_j t}) \qquad j = 1,2,3 \text{ and } 4 \tag{10}$$

Therefore,

$$\frac{dm_3}{dt} = L_3 X_3 e^{-X_3 t} \qquad \text{and} \tag{10a}$$

$$\frac{dm_4}{dt} = L_4 X_4 e^{-X_4 t}$$

and

$$m_3 = L_3(1-e^{-X_3 t}) \qquad \text{and} \tag{11}$$

$$m_4 = L_4(1-e^{-X_4 t})$$

From (11) we can write

$$\frac{m_4}{m_3} = \frac{L_4(1-e^{-X_4 t})}{L_3(1-e^{-X_3 t})} \tag{12}$$

which on simplification gives

$$\frac{m_4}{m_3} = \frac{L_4\left(X_4 t - \frac{(X_4 t)^2}{2!} + \ldots\right)}{L_3\left(X_3 t - \frac{(X_3 t)^2}{2!} + \ldots\right)} \qquad (13)$$

Ives and Hirth (5) measured pit widths as a function of etching time. Their results as obtained for dissolution of LiF in the etchant obtained by adding 2.5 ppm ferric ion as ferric fluoride to distilled water which had been slightly acidified to prevent the precipitation of ferric hydroxide, are shown in Figure 8. At 32°C in the linear region, it was estimated that 25 microns pit width took place in 5 minutes, and in 6×10^{-3} seconds only one atomic layer (4×10^{-8} cm) was removed from the pit. Assume the pit to have a square shape, $\sim 10^{13}$ particles were removed in 6×10^{-3} seconds from the pit surface. X_j are also very small since μ_j and λ_j are fractions. To a first approximation, then we can write

$$X_j t - \frac{(X_j t)^2}{2!} + \ldots \sim X_j t \qquad j = 3,4$$

and (13) becomes

$$\frac{m_4}{m_3} = \frac{L_4 X_4}{L_3 X_3}$$

which says $\frac{m_4}{m_3}$ will have a constant value for any pit shape, and it can be said that the value of m_4/m_3 depends upon the values of X_4 and X_3. From (10a), the rate of change of kink and in-ledge sites reduces with time till it becomes zero or is always zero depending on whether X_3 and X_4 are greater than zero or X_3 and X_4 are equal to zero. As discussed before for this case, X_3 and X_4 can never be negative. From (11) we can put down the three possible cases in Table 2.

B. Surface with System of Steps

The steps on the surface can give rise to different surface conditions at time t = 0. The dissolution from the surface now takes place by the movement of the steps and nucleation is not the limiting process. In general, we can say that $a_3 \neq 0$, $a_4 \neq 0$ and although $a_5 \neq A$, it is greater than L_5. For the kink and in-ledge sites following surface conditions could be possible

$$a_j > L_j \ , \ a_j < L_j \text{ and } a_j = L_j \qquad j = 3,4$$

In general from (8) we can write

$$m_3 = L_3 + (a_3 - L_3)\, e^{-X_3 t}$$

$$m_4 = L_4 + (a_4 - L_4)\, e^{-X_4 t}$$

As discussed for the case of perfect surface, to a first approximation, we can write

$$\left.\begin{aligned} m_3 &= a_3 + (L_3 - a_3)\, X_3 t \\ \text{and} \qquad m_4 &= a_4 + (L_4 - a_4)\, X_4 t \end{aligned}\right\} \qquad (15)$$

The rate of change of kink and in-ledge sites is

$$\left.\begin{aligned} \frac{dm_3}{dt} &= (L_3 - a_3)\, X_3 \\ \text{and} \qquad \frac{dm_4}{dt} &= (L_4 - a_4)\, X_4 \end{aligned}\right\} \qquad (16)$$

Following different cases can be obtained from (15) and (16).

1. For $X_3 < 0$ and $X_4 < 0$

The surface condition which is applicable in this case is $a_3 > L_3$ and $a_4 > L_4$, then from (15)

$$\frac{m_4}{m_3} = \frac{a_4 + (L_4 - a_4) X_4 t}{a_3 + (L_3 - a_3) X_3 t}$$

$$= \frac{\frac{a_4}{a_3}\left[\frac{a_3}{(L_3 - a_3)X_3 t} + Q\frac{a_3}{a_4}\right]}{\left[\frac{a_3}{(L_3 - a_3)X_3 t} + 1\right]} \qquad (17)$$

where $Q = \frac{dm_4}{dt} / \frac{dm_3}{dt}$

When the steps are already present on the surface in the form of a hole, then for a 25μ hole, there are $\sim 10^{13}$ particles on the steps of the hole. On this basis, $m_3 \sim a_3$ and $m_4 \sim a_4$ and (17) transforms to $\frac{m_4}{m_3} = Q$ and from (16) Q is

$$Q = \frac{(L_4 - a_4)X_4}{(L_3 - a_3)X_3}$$

Different pit shapes can be obtained depending on the value of Q.

2. For $X_3 < 0$ and $X_4 > 0$

The surface conditions which are applicable are $a_3 > L_3$ and $a_4 \gtrless L_4$. Then from (15)

$$m_3(t) = L_3 + (a_3 - L_3)(1 - X_3 t)$$

and

$$m_4 = L_4$$

when t is large irrespective of whether $a_4 > L_4$ or $a_4 < L_4$.

Under the condition $X_3 < 0$ and $a_3 > L_3$, $m_3(t)$ increases with time. When $a_4 > L_4$, and $X_4 > 0$, the mean population of in-ledge sites decreases with time, and becomes constant at large time and reverse is possible when $a_4 < L_4$ and $X_4 > 0$. Then we can write $\frac{m_4}{m_3}$ tends to zero when t tends to a large value.

3. For $X_3 > 0$ and $X_4 < 0$

The surface conditions which are applicable are $a_3 \gtrless L_3$ and $a_4 > L_4$. Then from (15) $m_3 = L_3$ when t is large irrespective of whether $a_3 > L_3$ or $a_3 < L_3$ and $m_4(t) = L_4 + (a_4 - L_4)(1-X_4t)$.

m_4 always increases with time. The ratio m_4/m_3 at large t is

$$\frac{m_4}{m_3} = \frac{L_4 + (a_4-L_4)(1-X_4t)}{L_3}$$

The value of $\frac{m_4}{m_3}$ tends to infinite as t tends to a large value.

4. There are cases when only one of the species increases with time and the other is constant at its value at t = 0. The results obtained in this case would be the same as in part (2) and part (3) above. When $a_3 > L_3$, $X_3 < 0$ and $a_4 = L_4$, $X_4 \lessgtr 0$, part (2) is applicable. When $a_3 = L_3$, $X_3 \lessgtr 0$ and $a_4 > L_4$, $X_4 < 0$, part (3) is applicable.

5. For $X_3 > 0$ and $X_4 > 0$

From (8), as t tends to a large value, irrespective of the surface condition ($a_3 \gtrless L_3$ and $a_4 \gtrless L_4$), we obtain

$$m_3 = L_3 \quad \text{and} \quad m_4 = L_4$$

which gives $\frac{m_4}{m_3} = \frac{L_4}{L_3}$. Substitute the values of $\frac{L_4}{L_3}$, we get,

$$\frac{m_4}{m_3} = \frac{\lambda_3 + \mu_3}{\lambda_4}$$

This is the condition that there is no net change in the population of kink sites on the surface. In other words, this case is obtained when there is dynamic equilibrium for dissolution.

There are other cases which lead to the dynamic equilibrium for dissolution, these cases and all the ones discussed above are summarized in Table 3. The cases marked with stars are of no importance to us and they in fact do not have any physical significance.

Until now we have only considered the conditions under which different pit shapes could be obtained, but we do not know what type of pit shapes will be obtained under different conditions. In order to understand this, for the pit shapes obtained in practice, we consider a simple cubic crystal with a single pit on its surface. As the results obtained above are for a pit of monoatomic depth, a pit of only monoatomic depth is considered. It is assumed that the atoms are only removed from the step sites. Our interest is only in kink and in-ledge sites. The aim is to find out how the population of the kink and in-ledge sites changes as the pit enlarges or as the time increases.

In Figures 9 to 14, different step systems in simple cubic crystal have been considered. The figures show the minimum size of the pit that could be obtained (the innermost shape) and it follows the pit shape as higher removal take place. In doing this, care was taken to see that the pit shape was perfect. It can be visualized that a particular perfect pit shape can have only a discrete number of removals from the surface. In Figures 9 to 14, the kink sites are marked with crosses.

For determining the number of kink and in-ledge sites on the surface as a function of total removal of atoms from the pit of a particular size, the following quantities are defined:

N_R is the total number of atoms removed from the surface for obtaining a pit of particular size. $N(C_3)$ is the number of kink atoms at the perfect pit and $N(C_4)$ is the number of in-ledge atoms at the perfect pit. Following the above analysis, it was seen that for a particular system of steps, for different dimensions of the pit, N_R is given as a polynomial of second order in degree L, where L is the number of the perfect pit obtained, the minimum sized pit being designated as L = 1.

In order to get a better quantitative picture, the values of $N(C_3)$, $N(C_4)$ and N_R were calculated as a function of L. The resulting formulae have been collected in Appendix IV. For the pit size parameter, a dimensionless quantity d_{rel} was chosen, which is defined as the ratio of the diameter of a sphere with a volume equal to N_R times the volume occupied by an atom in the unit cell, to an atom diameter d_{at}. Therefore,

$$d_{rel} = \frac{d_{sphere}}{d_{at}}$$

$$= \frac{1}{d_{at}} \left(\frac{6}{\pi} N_R \frac{V_u}{N_u}\right)^{1/3}$$

where V_u = volume of the unit cell

N_u = number of atoms in the unit cell.

For simple cubic crystal $n_u = 1$ and $V_u = d^3_{at}$, which gives

$$d_{rel} = \left(\frac{6}{\pi} N_R\right)^{1/3} = 1.241 \, (N_R)^{1/3}$$

hence d_{rel} for simple cubic crystal is only dependent on the number of atoms removed from the pit. Figures 15 to 20 show the results as obtained in the form of a plot of $N(C_3)$, $N(C_4)$ and $N(C_4)/N(C_3)$ versus d_{rel}. It is evident from these plots that $N(C_4)/N(C_3)$ reaches a limiting value of $\bar{K}$ as d_{rel} increases or as time increases. Table 4 gives the summary of the results as obtained from Figures 15 to 20 and Table 5 gives the value of $\bar{K}$ for the different step systems. In the results shown in Table 4, a little modification has been made for the step system (100) [010]. In actual cases for this step system , there are always a finite number of kinks at the pit and their time average can be taken as constant. Then we can say that $N(C_4)/N(C_3)$ increases with time for the system (100) [010].

Comparison of Table 3 and Table 5 gives the following conditions (Table 6) which are necessary for obtaining the corresponding pit shapes in the case of surface with steps.

Having obtained the rough conditions for which different pit shapes are formed, our next aim is to find the exact values of X_3 and X_4 or in other words, λ_j and μ_j's for which different pit shapes are formed. For this, computer analysis was carried out. Our endeavour in this respect was to find the extent to which computer analysis could be used in obtaining λ_j and μ_j's.

Computer Analysis

In the analysis that follows, we make the basic assumption that the dissolution of a crystal occurs by dissolution of characteristic sites at particular points on the crystal surface as defined by the TLK model. It is considered that the dissolution takes place from the characteristic sites irrespective of the molecule that is present at that point.

Depending on the sites the molecules occupy, the molecules on the surface are bound with different energies. It is also assumed that the forces of interactions of only the first neighbours are present. In keeping with the mathematical model, the line imperfections are neglected and also surface diffusion is neglected.

The problem of dissolution of surface from characteristic sites can be reduced in the following way. The source of steps taken is a two-dimensional hole in the surface layer of the crystal of monoatomic thickness. The hole at t=0 can have any shape or in other words, it can have any distribution of characteristic sites. The atoms from the characteristic site can be removed one at a time according to a set of predefined probabilities called the overall probabilities and designated as $e(C_j)$ where j = 1,2,3,4 and 5 for the respective characteristic sites. It means that the removal of the characteristic sites from the surface takes place at discrete moments of time. The removal of any characteristic site from the surface modifies the distribution of the other characteristic sites. For example, if a C_5 site comes out, it produces four sites of C_4 type, which are formed from four C_5 sites. In order to remove any characteristic site, we will have to know the ease with which this characteristic site could be removed with respect to all the other characteristic sites on the surface. This makes it essential for us to know the count of the characteristic sites of each type on the surface after each removal of a particular characteristic site. If $\bar{n}(C_j)$ denotes the number of characteristic sites of type C_j on the surface at any moment, then the probability that any one type of characteristic site is removed before the others, or at that moment, is given by

$$P(C_j) = \frac{\bar{n}\,(C_j)\, e(C_j)}{\sum_{j=1}^{5} \bar{n}(C_j)\, e(C_j)} \qquad j=1,2,3,4 \text{ and } 5 \qquad (18)$$

Computer Simulation

The computer simulation of crystal dissolution from atomic sites was carried out in the following way: The surface was mapped onto a square array, the integers contained in each element of the array indicating the layer of the crystal exposed to the surface. Steps are present if adjacent places contain different numbers. The uppermost layer of the crystal to begin with is designated as 1. The program made use of the periodic boundary conditions in attachment of particles not only from row to row within a single layer, but also from layer to layer, the last row in one layer was regarded as a neighbour to the first row in the next layer. Each row and layer consisted of 49 particles each way. No limitation to the number of layers was built in the program. Geometrically, this crystal under the periodic boundary conditions gives a toroidal shape to the surface. Before starting a run, the shape of the monoatomic hole in the first surface layer was decided and was built in the program.

The overall probabilities for each of the characteristic sites were selected at the beginning of each run. In the beginning of the process, the characteristic sites of each type were counted on the surface and the instantaneous probabilities $P(C_j)$ were calculated. The choice of the random outcome as to which characteristic site was to be removed was made by using Monte Carlo Method (15,16,17) (Appendix V), which utilises the random number generator operating in the unit interval (0,1)

(see Appendix V). Once the characteristic site (C_j) to be removed was decided, a decision was required as to which one of the characteristic sites out of a total of $\bar{n}(C_j)$ sites existing on the surface is to be removed. The choice of this random outcome was made again by a random number generator operating in the unit interval (0,1) (see Appendix V). At this stage, the integer contained in the element representing the characteristic site chosen by the above process was increased by one, to signify that the characteristic site has dissolved. Due to this removal, the adjacent characteristic sites to this characteristic site will have their coordination number lowered by one and these numbers of characteristic sites are deleted from $\bar{n}(C_j)$ and added to $\bar{n}(C_j\text{-}1)$. This gave the new count of the type of characteristic sites C_j and the whole process was repeated until a predetermined number of atom removals took place from the surface. Appendix VI gives the flow chart of the randomized model and Appendix VII gives the computer programme written in Fortran IV language. The program was run on CDC 3600 computer and it took about 11 seconds for 400 atom removals from the surface.

The dependence of the pit shape on the overall probabilities was determined in the experiments. In all the experiments $e(C_1)$, $e(C_2)$ and $e(C_5)$ were given the same value. The overall probability of the ad-atom site will be highest since it is bound on the surface with the least energy as compared to other characteristic sites and since we are neglecting surface diffusion, we want all the ad-atom sites to dissolve as soon as they form. On this basis, the value of $e(C_1)$ chosen was 1.0. On similar grounds $e(C_2)$= 0.1. The removal of in-terrace sites is dependent on $e(C_5)$, that is the nucleation on the surface at new sites is dependent on $e(C_5)$.

As we are dealing with a very small surface, and we are interested only in seeing the development of the pit with time, it is necessary to restrict the value of $e(C_5)$ to a low value so that no surface nucleation takes place. The value of $e(C_5)$ taken was 1×10^{-12}. The important variables are overall probabilities of kink and in-ledge sites. It was observed that the variations of $e(C_3)$ or $e(C_4)$ does not make any difference to the observed morphology on the surface as far as $e(C_3)/e(C_4)$ had a constant value. On this basis, we also gave $e(C_4)$ a constant value and varied only $e(C_3)$. The value of $e(C_4)$ should be such that $e(C_3)$ could be varied over a large range. The value of $e(C_4)$ so chosen was 1.0×10^{-5}. The value of $e(C_3)$ was then varied from 1.0 to 2×10^{-6}.

RESULTS

As mentioned previously, the configuration at the pit does not vary as long as the ratio $e(C_3)/e(C_4)$ is constant irrespective of the values of $e(C_3)$ and $e(C_4)$. Thus instead of using $e(C_3)$ and $e(C_4)$, we will use a new notation $e_{34} = e(C_3)/e(C_4)$ which gives a better physical picture. Physically, e_{34} is the relative probability of removal of kink sites with respect to the inledge sites.

For each of the e_{34} values twenty experiments were carried out. The number of experiments was limited to twenty because of the fact that for the same input parameters the spread in the values of SITE (j) between experiments was very small. In the case of each of these twenty experiments, the starting random number for the string of the random number generator was different. This was necessary for complete randomization of the process. After each removal SITE (j) values were noted and for each experiment for a particular value of e_{34}, the sample mean of SITE(j) was obtained for 365 removals. The sample mean has been denoted as $(SITE_j)$ for

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for the jth characteristic site. The population mean was obtained for each value of e_{34} from the sample means of twenty experiments. The population mean has been denoted as $(SITE_j)$ av.

The values of $(SITE_3)$ av. are plotted against the square root of e_{34} for each value of e_{34} as shown in figure 21. It is observed from this figure that $(SITE_3)$av. has a limiting value of 0.003.

The structure of the pits are seen in figure 22 and 23, which are reproductions of the computer's printed output and show the locations of the atoms on the lattice surface. Numeral 1 stands for the particles in the first surface layer and numeral 2 stands for the particles in the layer just beneath the first surface layer. The lines drawn across the crystal indicate the boundary between the particles of the first and the second layer which are exposed to the medium and actually show the structure of the pit surface. Figure 22(a) and 23(a) show the portions of the crystal surface at t = 0. Figures 22(b) and 23(b) show the same portions after 365 removals for $e(C_3)$ = 0.01. Also figures 22(c) and 23(c) show the portion of the crystal surface in 22(a) and 23(a) after 365 removals for $e(C_3) = 1.0 \times 10^{-4}$. It is seen from the figures that irrespective of the initial shape of the hole or the initial distribution of the different characteristic sites on the surface, the end result for the same values of $e(C_3)$ is the same. When $e(C_3)$ = 0.01, the (100) [010] step system is obtained for the pit but when $e(C_3) = 1.0 \times 10^{-4}$ there is no regular pattern at the pit surface and the configuration is rough.

DISCUSSION:

It is observed from figures 22 and 23 that irrespective of the initial shape of the hole or the initial distribution of the different characteristic sites on the surface, the end result for the same values of e_{34} is

the same. This is the Morkoffian property on which the mathematical model is based. On the basis of this property, it seems that the computer simulation is representative of the mathematical model.

As observed in the last section there is a limiting value of 0.003 for $(SITE_3)$ av. The reason why the limiting value of $(SITE_3)$ av. stays finite is that there are always a finite number of kink sites on the surface at any time. During the dissolution process the formation of kink sites takes place by the removal of the in-ledge sites from the steps. The major part of the dissolution then takes place by the motion of the kink sites thus formed. If there is no formation of kink sites on the surface, then the dissolution cannot take place. Hence, for dissolution to proceed, there must be finite number of kink sites on the step surface.

There are three ranges of behaviour of $(SITE_3)$ av. with e_{34}.

(i) $\sqrt{e_{34}} > 50.0$, the value of $(SITE_3)$ av. hardly increases at all with e_{34} i.e. $(SITE_3)$av. is independent of e_{34}. This is the range where square morphology is obtained. At any moment the number of kink sites on the surface is very small. If at any instant there are no kink sites on the step, immediately an inledge site comes out to form two kink sites. The small number of kink sites helps to maintain the (100)[010] step system at the pit.

(ii) $\sqrt{e_{34}} < 3.0$, $(SITE_3)$ av. varies linearly with e_{34} in this range. This is the range where rough morphology is obtained.

(iii) $3.0 < \sqrt{e_{34}} < 50.0$, this is the intermediate range.

It is clear from the above that if the process variables are such that $\sqrt{e_{34}} > 50.0$, then the step system obtained will always be (100) [010].

As mentioned before, for the simulation only one set of numbers, the overall probabilities were used as the input parameters. These probabi-

lities were fixed throughout the simulation experiment. It means that the simulation was carried on for the deterministic model. In fact the input information we have put in the simulation part is not complete and is not representative of the mathematical model. This is so because of the fact that the mathematical model is probabilistic and not deterministic. We are completely neglecting the chance variations which are part of the mathematical model.

The simulation was carried on for the deterministic model because up to now, it has not been possible to find the form of the distributions for the different characteristic sites. Once the form of the distributions for the different characteristic sites is known, we will be in a position to have two sets of numbers as the input parameters. The two sets of numbers will be (i) the mean and (ii) the standard deviation of the distribution function for each of the characteristic site. The overall effect of this would be that we will have different values of overall probabilities for each of the characteristic sites after each removal of any characteristic site.

As mentioned before we have been able to obtain only the rough morphology and the morphology with (100)[010] system of steps during the computer simulation experiment. Up to now, it has not been possible to obtain the (100)[110] system of steps during the computer simulation experiment. A glance at the input information tells that the enthalpy and vibrational entropy are accounted for by the values of the overall probabilities whereas the configurational entropy is accounted for by the crystal matrix. The configurational entropy control will then be possible - provided we include back flow in the simulation experiment.

Inclusion of back flow in the simulation experiment means that we should take into account migration of the atoms on the surface. We assign

probabilities for the movement of the atoms towards East, West, South or North. In the simplest experiment we assign equal probabilities for all four directions and the atom site selected is allowed to move towards the direction selected by unit distance. We do not let the in-terrace, in-ledge, kink and ad-atom sites to be removed directly from the surface, but instead all these sites are transformed consequently to lower coordination number sites and removal of an atom from the surface takes place only when it forms an adatom site.

Also as we approach the step system (100)[110], the positions of kinks in the steps are no longer the kinks of unit height as is the case for the system (100)[010]. This is because of the influence of the second nearest neighbor bonds. We can include the second nearest neighbour bonds for the kink sites in the simulation experiment. Two type of kink sites are obtained on the basis that the number of the second nearest neighbours for them is different. On this basis we have to define one more overall probability parameter as the input parameter.

CONCLUSIONS

1. The differential difference equation obtained by the stochastic development of the model, has been solved exactly for pits of monoatomic thickness.

2. With the help of geometric considerations for the pits of the type (100)[010], (100)[011] and (100)[010] and (100)[011] and the results of the model, some of the necessary conditions for obtaining the corresponding pit shapes have been obtained.

3. Computer simulation has been carried out to find the extent to which it could be used. It seems that with the additional information of the form of the distribution of the different characteristic sites and the modification of the experiment to take into account the back flow and the second

nearest neighbour bonds, one should be able to find the conditions under which different pit shapes are obtained. This should be the next aspect of the simulation to be considered.

References

1. W. K. Burton, N. Cabrera and F. C. Frank, Phil. Trans. Roy. Soc. 243A, London, p. 299 (1951).
2. F. C. Frank, in "Growth and Perfection of Crystals", eds. R. H. Doremus, B. W. Roberts and D. Turnbull, John Wiley, New York (1958) p. 411.
3. W. Kossel, Nachr. Ges Wiss Gottingen, Math. Physik., Klasse, p. 135 (1927).
4. I. N. Stranski, Z. Physik Chem. 136, 259 (1928); 11, 421 (1931).
5. M. B. Ives and J. P. Hirth, J. Chem. Phys. 33, 517 (1960).
6. V. N. Rozhanskii, E. V. Parvova, V. M. Stepanova and A. A. Prednoditelev, Kristallogr. 6, 704 (1961); English translation in Sov. Phys. - Crystallogr. 6, 564 (1962).
7. N. F. Kostin, S. V. Lubenets and K. S. Alexsandrov, Kristallogr. 6, 737 (1961); English translation in Sov. Phys. - Crystallogr. 6, 588 (1962).
8. M. B. Ives, J. Phys. and Chem. of Solids, 24, 2, 275 (1963).
9. A. J. W. Moore, J. Austral. Inst. Metals. 11, 220 (1966).
10. A. A. Chernov, in "Crystal Growth", ed. S. Peiser, Pergamon (1967), p. 25.
11. A. A. Chernov and J. Lewis, J. Phys. Chem. Solids 28, 2185 (1967).
12. U. Bertocci, Surface Science 15, 2, 286 (1969).
13. J. F. Nicholas, An Atlas of Models of Crystal Surfaces, Gordon and Breach, New York (1965).
14. W. Feller, "An Introduction to Probability Theory and Its Applications", vol. I, John Wiley and Sons (1968).
15. Yu. A. Schreider, "The Monte Carlo Method", Pergamon Press, New York (1966).
16. E. D. Cashwell and C. J. Everett, "A Practical Manual of Monte Carlo Method", Pergamon Press, New York (1959).

References (continued)

17. F. F. Martin, "Computer Modelling and Simulation", John Wiley & Sons, New York (1968).

APPENDIX I

To Find Differential Equations in Terms of the Mean Value of the Fraction of Each Characteristic Site

Starting with the differential equation

$$\frac{\partial P}{\partial t} = \sum_{j=2}^{5} \lambda_j (x_{j-1} - x_j) \frac{\partial P}{\partial x_j} + \sum_{j=1}^{4} \mu_j (x_5 - x_j) \frac{\partial P}{\partial x_j} \qquad (3)$$

and the boundary conditions

$$P\begin{pmatrix} x_5 \\ x_4 \\ x_3 \\ x_2 \\ x_1 \end{pmatrix}, t = x_1^{a1} x_2^{a2} x_3^{a3} x_4^{a4} x_5^{a5} \qquad (4)$$

where P is the generating function, we write $x_j = e^{\Theta j}$ which gives the corresponding moment generating function.

$$M\begin{pmatrix} \Theta_5 \\ \Theta_4 \\ \Theta_3 \\ \Theta_2 \\ \Theta_1 \end{pmatrix}, t = P\begin{pmatrix} e^{\Theta 5} \\ e^{\theta 4} \\ e^{\Theta 3} \\ e^{\Theta 2} \\ e^{\Theta 1} \end{pmatrix}, t \qquad (A1)$$

then (3) and (4) become

$$\frac{\partial M}{\partial t} = \sum_{j=2}^{5} \lambda_j \left(e^{-\Theta_j + \Theta_{j-1}} - 1\right) \frac{\partial M}{\partial \Theta_j} + \sum_{j=1}^{4} \mu_j \left(e^{-\Theta_j + \Theta_5} - 1\right) \frac{\partial M}{\partial \Theta_j} \qquad (A2)$$

with initial condition

$$M\left(\begin{matrix}\theta_5\\ \theta_4\\ \theta_3\\ \theta_2\\ \theta_1\end{matrix}, 0\right) = e^{(a_1\theta_1 + a_2\theta_2 + a_3\theta_3 + a_4\theta_4 + a_5\theta_5)} \qquad (A3)$$

Taking logarithm of (A1) gives the cumulant generating function

$$K\left(\begin{matrix}\theta_5\\ \theta_4\\ \theta_3\\ \theta_2\\ \theta_1\end{matrix}, t\right) = \log M\left(\begin{matrix}\theta_5\\ \theta_4\\ \theta_3\\ \theta_2\\ \theta_1\end{matrix}, t\right) = \log P\left(\begin{matrix}e^{\theta 5}\\ e^{\theta 4}\\ e^{\theta 3}\\ e^{\theta 2}\\ e^{\theta 1}\end{matrix}, t\right) \qquad (A4)$$

Then (A2) and (A3) become

$$\frac{\partial K}{\partial t} = \sum_{j=2}^{5} \lambda_j \left(e^{-\theta_j+\theta_{j-1}} - 1\right) \frac{\partial K}{\partial \theta_j} + \sum_{j=1}^{4} \mu_j \left(e^{-\theta_j+\theta_5} - 1\right) \frac{\partial K}{\partial \theta_j} \qquad (A5)$$

with the initial condition

$$K\left(\begin{matrix}\theta_5\\ \theta_4\\ \theta_3\\ \theta_2\\ \theta_1\end{matrix}, 0\right) = a_1\theta_1 + a_2\theta_2 + a_3\theta_3 + a_4\theta_4 + a_5\theta_5 \qquad (A6)$$

In order to find the mean values of the numbers of different characteristic sites, it is necessary to expand the cumulant generating function in (A5) in first powers of θ_1, θ_2, θ_3, θ_4 and θ_5. To achieve this, the value of cumulant generating function must be known in terms of

θ_1, θ_2, θ_3, θ_4 and θ_5 i.e. for the five random variables, we are concerned with the joint probability distribution at time t given by

$$P\{ x_1(t) = b,\ x_2(t) = c,\ x_3(t) = d,\ x_4(t) = e,\ x_5(t) = f \} = p_{bcdef}(t) \tag{A7}$$

for which we can define the probability generating function

$$P\left(\begin{matrix} x_5 \\ x_4 \\ x_3 \\ x_2 \\ x_1 \end{matrix}, t\right) = \sum_{b,c,d,e,f} p_{bcdef}(t)\ x_1^{\,b}\ x_2^{\,c}\ x_3^{\,d}\ x_4^{\,e}\ x_5^{\,f} \tag{A8}$$

Applying (A1), we can write the moment generating function

$$M\left(\begin{matrix} \theta_5 \\ \theta_4 \\ \theta_3 \\ \theta_2 \\ \theta_1 \end{matrix}, t\right) = \sum_{b,c,d,e,f} p_{bcdef}(t)\ e^{b\theta_1+c\theta_2+d\theta_3+e\theta_4+f\theta_5} \tag{A9}$$

and applying (A4) gives the cumulant generating function

$$K\left(\begin{matrix} \theta_5 \\ \theta_4 \\ \theta_3 \\ \theta_2 \\ \theta_1 \end{matrix}, t\right) = \log \sum_{b,c,d,e,f} p_{bcdef}(t)\ e^{b\theta_1+c\theta_2+d\theta_3+e\theta_4+f\theta_5} \tag{A10}$$

Expanding

$$K\left(\begin{matrix} \theta_5 \\ \theta_4 \\ \theta_3 \\ \theta_2 \\ \theta_1 \end{matrix}, t\right)$$

in powers of θ_1, θ_2, θ_3, θ_4 and θ_5 provides the definition in terms of joint cumulants as

$$K\begin{pmatrix}\theta_5\\ \theta_4\\ \theta_3\\ \theta_2\\ \theta_1\end{pmatrix}, t = \sum_{u,v,w,x,y\geq 0}^{\infty} k_{uvwxy}(t)\,\frac{\theta_1^{\,u}\,\theta_2^{\,v}\,\theta_3^{\,w}\,\theta_4^{\,x}\,\theta_5^{\,y}}{u!\;v!\;w!\;x!\;y!} \qquad \text{(A11)}$$

where $k_{00000} = 0$.

Using (A11) in (A5) and equating the coefficients of θ_j on both sides of (A5), the following differential equations are obtained

$$\frac{dm_1(t)}{dt} = -\mu_1 m_1(t) + \lambda_2 m_2(t)$$

$$\frac{dm_2(t)}{dt} = -(\lambda_2+\mu_2)\, m_2(t) + \lambda_3 m_3(t)$$

$$\frac{dm_3(t)}{dt} = -(\lambda_3+\mu_3)\, m_3(t) + \lambda_4 m_4(t)$$

$$\frac{dm_4(t)}{dt} = -(\lambda_4+\mu_4)\, m_4(t) + \lambda_5 m_5(t)$$

$$\frac{dm_5(t)}{dt} = -\lambda_5 m_5(t)+\mu_1 m_1(t)+\mu_2 m_2(t)+\mu_3 m_3(t)+\mu_4 m_4(t)$$

where $k_{10000} = m_1$, $k_{01000} = m_2$, $k_{00100} = m_3$, $k_{00010} = m_4$ and $k_{00001} = m_5$.

APPENDIX II

Solution of System of Differential Equations

The differential equations are:

$$\frac{dm_1(t)}{dt} = -\mu_1 m_1(t) + \lambda_2 m_2(t) \qquad (B1)$$

$$\frac{dm_2(t)}{dt} = -(\lambda_2+\mu_2)\, m_2\,(t) + \lambda_3 m_3(t) \qquad (B2)$$

$$\frac{dm_3(t)}{dt} = -(\lambda_3+\mu_3)\, m_3\,(t) + \lambda_4 m_4(t) \qquad (B3)$$

$$\frac{dm_4(t)}{dt} = -(\lambda_4+\mu_4)\, m_4\,(t) + \lambda_5 m_5(t) \qquad (B4)$$

$$\frac{dm_5(t)}{dt} = -\lambda_5 m_5(t) + \mu_1 m_1(t) + \mu_2 m_2(t) + \mu_3 m_3(t) + \mu_4 m_4(t) \qquad (B5)$$

with the initial conditions

$$m_j(0) = a_j \qquad j = 1,2,3,4 \text{ and } 5 \qquad (B6)$$

The solution of these equations can be obtained as follows:

Let $Q_j(s) = L\{m_j(t)\}$ denote the Laplace transform of $m_j(t)$, then the subsidiary system of equations is given by:

$$\left.\begin{aligned}
(\mu_1+s)\, Q_1(s) - \lambda_2 Q_2(s) &= a_1 \\
(\mu_2+\lambda_2+S)Q_2(s) - \lambda_3 Q_3(s) &= a_2 \\
(\mu_3+\lambda_3+s)Q_3(s) - \lambda_4 Q_4(s) &= a_3 \\
(\mu_4+\lambda_4+s)Q_4(s) - \lambda_5 Q_5(s) &= a_4
\end{aligned}\right\}$$

$$(\lambda_5+s)Q_5(s) - \mu_1Q_1(s)-\mu_2Q_2(s)-\mu_3Q_3(s)-\mu_4Q_4(s) = a_5 \Big\rfloor \quad (B7)$$

The above is a set of simultaneous equations whose determimant can be written down as

$$D = \begin{vmatrix} \mu_1+s & -\lambda_2 & 0 & 0 & 0 \\ 0 & \mu_2+\lambda_2+s & -\lambda_3 & 0 & 0 \\ 0 & 0 & \mu_3+\lambda_3+s & -\lambda_4 & 0 \\ 0 & 0 & 0 & \mu_4+\lambda_4+s & -\lambda_5 \\ -\mu_1 & -\mu_2 & -\mu_3 & -\mu_4 & \lambda_5+s \end{vmatrix}$$

Solving the system of algebraic equations (B7) we have

$$Q_1(s) = \frac{\begin{vmatrix} a_1 & -\lambda_2 & 0 & 0 & 0 \\ a_2 & \mu_2+\lambda_2+s & -\lambda_3 & 0 & 0 \\ a_3 & 0 & \mu_3+\lambda_3+s & -\lambda_4 & 0 \\ a_4 & 0 & 0 & \mu_4+\lambda_4+s & -\lambda_5 \\ a_5 & -\mu_2 & -\mu_3 & -\mu_4 & \lambda_5+s \end{vmatrix}}{D}$$

$$Q_2(s) = \frac{\begin{vmatrix} \mu_1+s & a_1 & 0 & 0 & 0 \\ 0 & a_2 & -\lambda_3 & 0 & 0 \\ 0 & a_3 & \mu_3+\lambda_3+s & -\lambda_4 & 0 \\ 0 & a_4 & 0 & \mu_4+\lambda_4+s & -\lambda_5 \\ -\mu_1 & a_5 & -\mu_3 & -\mu_4 & \lambda_5+s \end{vmatrix}}{D}$$

$$Q_3(s) = \frac{\begin{vmatrix} \mu_1+s & -\lambda_2 & a_1 & 0 & 0 \\ 0 & \mu_2+\lambda_2+s & a_2 & 0 & 0 \\ 0 & 0 & a_3 & -\lambda_4 & 0 \\ 0 & 0 & a_4 & \mu_4+\lambda_4+s & -\lambda_5 \\ -\mu_1 & -\mu_2 & a_5 & -\mu_4 & \lambda_5+s \end{vmatrix}}{D}$$

$$Q_4(s) = \frac{\begin{vmatrix} \mu_1+s & -\lambda_2 & 0 & a_1 & 0 \\ 0 & \mu_2+\lambda_2+s & -\lambda_3 & a_2 & 0 \\ 0 & 0 & \mu_3+\lambda_3+s & a_3 & 0 \\ 0 & 0 & 0 & a_4 & -\lambda_5 \\ -\mu_1 & -\mu_2 & -\mu_3 & a_5 & \lambda_5+s \end{vmatrix}}{D}$$

$$Q_5(s) = \frac{\begin{vmatrix} \mu_1+s & -\lambda_2 & 0 & 0 & a_1 \\ 0 & \mu_2+\lambda_2+s & -\lambda_3 & 0 & a_2 \\ 0 & 0 & \mu_3+\lambda_3+s & -\lambda_4 & a_3 \\ 0 & 0 & 0 & \mu_4+\lambda_4+s & a_4 \\ -\mu_1 & -\mu_2 & -\mu_3 & -\mu_4 & a_5 \end{vmatrix}}{D}$$

In each of the above the degree of the numerator is less than the degree of the denominator and hence we can expand in partial fractions to obtain a solution of the form

$$Q_i(s) = \sum_{j=1}^{5} \frac{c_{ij}}{s-s_j} \qquad i = 1,2,3,4,5$$

where $s_1, s_2 \ldots s_5$ are the roots of the determimant D, and the c_{ij} are constants.

The determinant D on evaluation gives

$$s^5 + s^4 (\lambda_5+\lambda_4+\mu_4+\lambda_3+\mu_3+\lambda_2+\mu_2+\mu_1)$$

$$+ s^3 [\lambda_5\lambda_4+\mu_1(\mu_2+\lambda_2)+(\mu_3+\lambda_3)(\mu_1+\mu_2+\lambda_2) + (\mu_4+\lambda_4+\lambda_5)(\mu_1+\mu_2+\lambda_2+\mu_3+\lambda_3)]$$

$$+ s^2 [\lambda_5\lambda_4(\lambda_3+\mu_1+\mu_2+\lambda_2)+\mu_1(\mu_2+\lambda_2)(\mu_3+\lambda_3) + (\mu_4+\lambda_4+\lambda_5)[\mu_1(\mu_1+\lambda_2)+(\mu_3+\lambda_3)(\mu_1+\mu_2+\lambda_2)]$$

$$+ s [\lambda_5\lambda_4(\lambda_3\mu_1+\lambda_3\lambda_2+\mu_1\mu_2+\lambda_2\mu_1) + \mu_1(\mu_1+\lambda_2)(\mu_3+\lambda_3)(\mu_4+\lambda_4+\lambda_5)] = 0 \qquad \text{(B8)}$$

It is clear from the above that $s = 0$ is one of the roots of the determinant and if s_1, s_2, s_3 and s_4 are the other roots, then

$$D = s(s-s_1)(s-s_2)(s-s_3)(s-s_4)$$

Taking out one s from (B8) we can see that obtaining the roots of the quartic is a formidable task. Hence numerical techniques have to be used to obtain the roots. Nonetheless, once we know the roots, we can apply the inverse transforms and obtain

$$m_j(t) = \sum_{i=1}^{4} c_{ij} \; e^{s_i t} + c_{j5} \qquad j = 1,2,3,4 \text{ and } 5$$

APPENDIX III

The Solution of System of Differential Equations

The differential equations are

$$\frac{dm_1(t)}{dt} = -\mu_1 m_1(t) + \lambda_2 m_2(t) \tag{C1}$$

$$\frac{dm_2(t)}{dt} = -(\lambda_2+\mu_2)m_2(t)+\lambda_3 m_3(t) \tag{C2}$$

$$\frac{dm_3(t)}{dt} = -(\lambda_3+\mu_3)m_3(t)+\lambda_4 m_4(t) \tag{C3}$$

$$\frac{dm_4(t)}{dt} = -(\lambda_4+\mu_4)m_4(t)+\lambda_5 m_5(t) \tag{C4}$$

$$\frac{dm_5(t)}{dt} = -\lambda_5 m_5(t)+\mu_1 m_1(t)+\mu_2 m_2(t)+\mu_3 m_3(t)+\mu_4 m_4(t) \tag{C5}$$

with the initial conditions

$$m_j(0) = a_j \qquad \text{where } j = 1,2,3,4 \text{ and } 5 \tag{C6}$$

The solution is to be obtained under the assumption

$$\sum_{j=1}^{5} m_j(t) = A \tag{C7}$$

From (C7) we can write

$$m_1 = A-m_2-m_3-m_4-m_5$$

Substituting the value of m_1 in (C5), we have

$$\frac{dm_5}{dt}(t) = \mu_1 A - (\mu_1-\mu_2)m_2-(\mu_1-\mu_3)m_3-(\mu_1-\mu_4)m_4-(\mu_1+\lambda_5)m_5 \qquad (C8)$$

The equations (C1) to (C4) and (C8) are a set of simultaneous equations. If we substitute in these equations

$$\frac{dm_j(t)}{dt} = Dm_j \qquad \text{where } j = 1,2,3,4 \text{ and } 5$$

i.e. $\frac{d}{dt} = D$, we get the following set of equations:

$$(D+\mu_1)m_1-\lambda_2 m_2+0m_3+0m_4+0m_5 = 0 \qquad (C9)$$

$$0m_1+(D+\lambda_2+\mu_2)m_2-\lambda_3 m_3+0m_4+0m_5 = 0 \qquad (C10)$$

$$0m_1+0m_2+(D+\lambda_3+\mu_3)m_3-\lambda_4 m_4+0m_5 = 0 \qquad (C11)$$

$$0m_1+0m_2+0m_3+(D+\lambda_4+\mu_4)m_4-\lambda_5 m_5 = 0 \qquad (C12)$$

$$0m_1+(\mu_1-\mu_2)m_2 + (\mu_1-\mu_3)m_3+(\mu_1-\mu_4)m_4+(D+\mu_1+\lambda_5)m_5 = \mu_1 A \qquad (C13)$$

The value of m_2, m_3, m_4 and m_5 can now be obtained by the use of the determinants from the last four simultaneous equations (C10) to (C13). Thus,

$$(C14) \quad \begin{vmatrix} D+\lambda_2+\mu_2 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_3 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & -\lambda_5 \\ \mu_1-\mu_2 & \mu_1-\mu_3 & \mu_1-\mu_4 & D+\mu_1+\lambda_5 \end{vmatrix} m_2(t) = \begin{vmatrix} 0 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_3 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & -\lambda_5 \\ \mu_1 A & \mu_1-\mu_3 & \mu_1-\mu_4 & D+\mu_1+\lambda_5 \end{vmatrix}$$

$$(C15)\quad \begin{vmatrix} D+\lambda_2+\mu_2 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_3 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & -\lambda_5 \\ \mu_1-\mu_2 & \mu_1-\mu_3 & \mu_1-\mu_4 & D+\mu_1+\lambda_5 \end{vmatrix} m_3(t) = \begin{vmatrix} D+\lambda_2+\mu_2 & 0 & 0 & 0 \\ 0 & 0 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & -\lambda_5 \\ \mu_1-\mu_2 & \mu_1 A & \mu_1-\mu_4 & D+\mu_1+\lambda_5 \end{vmatrix}$$

$$(C16)\quad \begin{vmatrix} D+\lambda_2+\mu_2 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_3 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & -\lambda_5 \\ \mu_1-\mu_2 & \mu_1-\mu_3 & \mu_1-\mu_4 & D+\mu_1+\lambda_5 \end{vmatrix} m_4(t) = \begin{vmatrix} D+\lambda_2+\mu_2 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_3 & 0 & 0 \\ 0 & 0 & 0 & -\lambda_5 \\ \mu_1-\mu_2 & \mu_1-\mu_3 & \mu_1 A & D+\mu_1+\lambda_5 \end{vmatrix}$$

$$C(17)\quad \begin{vmatrix} D+\lambda_2+\mu_2 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_3 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & -\lambda_5 \\ \mu_1-\mu_2 & \mu_1-\mu_3 & \mu_1-\mu_4 & D+\mu_1+\lambda_5 \end{vmatrix} m_5(t) = \begin{vmatrix} D+\lambda_2+\mu_2 & -\lambda_3 & 0 & 0 \\ 0 & D+\lambda_3+\mu_4 & -\lambda_4 & 0 \\ 0 & 0 & D+\lambda_4+\mu_4 & 0 \\ \mu_1-\mu_2 & \mu_1-\mu_3 & \mu_1-\mu_4 & \mu_1 A \end{vmatrix}$$

Solving the determinants in (C14) to(C17) we get the following equations:

$$\{[(D+\lambda_2+\mu_2)(D+\lambda_3+\mu_3)\{(D+\lambda_4+\mu_4)(D+\mu_1+\lambda_5) + (\mu_1-\mu_4)\lambda_5\} + \lambda_4\{\lambda_5(\mu_1-\mu_3)\}] + \lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)\}m_2 = \lambda_3\lambda_4\lambda_5\mu_1 A \qquad (C18)$$

$$\{[(D+\lambda_2+\mu_2)(D+\lambda_3+\mu_3)\{(D+\mu_4+\lambda_4)(D+\mu_1+\lambda_5) + (\mu_i-\mu_4)\lambda_5\} + \lambda_4\{\lambda_5(\mu_1-\mu_3)\}] + \lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)\}m_3 = \lambda_4\lambda_5(\lambda_2+\mu_2)\mu_1 A \qquad (C19)$$

$$\{[(D+\lambda_2+\mu_2)(D+\lambda_3+\mu_3)\{(D+\lambda_4+\mu_4)(D+\mu_1+\lambda_5) + (\mu_1-\mu_4)\lambda_5\} +$$

$$\lambda_4\{\lambda_5(\mu_1-\mu_3)\}] + \lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)\}m_4$$

$$= \lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)\mu_1 A \qquad (C20)$$

$$\{[(D+\lambda_2+\mu_2)(D+\lambda_3+\mu_3)\{(D+\lambda_4+\mu_4)(D+\mu_1+\lambda_5) + (\mu_1-\mu_4)\lambda_5\} +$$

$$\lambda_4\{\lambda_5(\mu_1-\mu_3)\}] + \lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)\}m_5$$

$$= (\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)\mu_1 A \qquad (C21)$$

In the above differential equations, we have now the variables separated. These are non-homogeneous differential linear equations. The general principle on which the solution of such type of equations is obtained is:

Any solution of a non-homogeneous linear equations L(m) = f is the sum of a particular solution of the non-homogeneous equation and a solution of the corresponding homogeneous equation (complementary function). Thus the solution can be written as

$$m = y_1 + v$$

where y_1 = particular solution

and v = a complementary function.

The equations (C18) to (C21) have power of 4 for D. There will be 4 constants in the complementary function for each of these equations, since there will be four roots of the homogeneous linear equation .

Thus the complementary function for equations (C18) to (C21) is

$$v = C_1 e^{At} + C_2 e^{Bt} + C_3 e^{Ct} + C_4 e^{Dt}$$

where A,B,C and D are the roots which can be obtained in terms of λ's μ's from the auxiliary polynomial

$$\{[(\gamma+\lambda_2+\mu_2)(\gamma+\lambda_3+\mu_3)\{(\gamma+\lambda_4+\mu_4)(\gamma+\mu_1+\lambda_5) + (\mu_1-\mu_4)\lambda_5\} +$$

$$\lambda_4\{\lambda_5(\mu_1-\mu_3)\}]+\lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)\} = 0$$

for the cases (C18) to (C21), and C_1,C_2,C_4 and C_4 are constants which will have the same values for cases (C18) to (C21).

The particular solution will be different for all of the differential equations (C18) to (C21) and can be obtained as

$$y_2' = \frac{1}{\left[\begin{array}{c}\{(D+\lambda_2+\mu_2)(D+\lambda_3+\mu_3)\{(D+\lambda_4+\mu_4)(D+\mu_1+\lambda_5) + (\mu_1-\mu_4)\lambda_5\} + \\ \lambda_4\{\lambda_5(\mu_1-\mu_3)\}] + \lambda_3\lambda_4\lambda_5\ (\mu_1-\mu_2)\}\end{array}\right]} \lambda_3\lambda_4\lambda_5\mu_1 e^{\circ t}$$

$\lambda_3\lambda_4\lambda_5\mu_1$ has been multiplied by $e^{\circ t}$ (since $e^{\circ t} = 1$) and by doing this, the calculation of particular solution becomes very simple. Now the procedure is to put down zero in the place of D and simplify the above. The final value obtained is the particular solution. Thus

$$y_2' = \frac{\lambda_3\lambda_4\lambda_5\mu_1 A}{N}$$

$$y_3' = \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)\mu_1 A}{N}$$

$$y_4' = \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)\mu_1 A}{N}$$

$$y_5' = \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)\mu_1 A}{N}$$

where $N = (\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)(\mu_1+\lambda_5) + (\lambda_2+\mu_2)(\lambda_3+\mu_3) \times$

$$(\mu_1-\mu_4)\lambda_5 + \lambda_4\lambda_5(\lambda_2+\mu_2)(\mu_1-\mu_3) + \lambda_3\lambda_4\lambda_5(\mu_1-\mu_2)$$

Now we can put down the final solution for (C18) to C21) as

$$m_2 = C_1e^{At} + C_2e^{Bt} + C_3e^{Ct} + C_4e^{Dt} + \frac{\lambda_3\lambda_4\lambda_5\mu_1A}{N} \qquad (C22)$$

$$m_3 = C_1e^{At} + C_2e^{Bt} + C_3e^{Ct} + C_4e^{Dt} + \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)\mu_1A}{N} \qquad (C23)$$

$$m_4 = C_1e^{At} + C_2e^{Bt} + C_3e^{Ct} + C_4e^{Dt} + \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)\mu_1A}{N} \qquad (C24)$$

$$m_5 = C_1e^{At} + C_2e^{Bt} + C_3e^{Ct} + C_4e^{Dt} + \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)\mu_1A}{N} \qquad (C25)$$

We want to get rid of C_1, C_2, C_3 and C_4; this can be done by substracting m_2 from m_3, m_3 from m_4 and m_4 from m_5. This choice was made so that the differences could be utilised for further solution. THus

$$m_3-m_2 = \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)\mu_1A-\lambda_3\lambda_4\lambda_5\mu_1A}{N}$$

$$= \frac{\lambda_4\lambda_5(\lambda_2+\mu_2-\lambda_3)\mu_1A}{N} \qquad (C26)$$

$$m_4-m_3 = \frac{\lambda_5(\lambda_2+\mu_2)[\lambda_3+\mu_3-\lambda_4]\mu_1A}{N} \qquad (C27)$$

$$m_5-m_4 = \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4-\lambda_5)\mu_1A}{N} \qquad (C28)$$

On rearranging these we can write

$$m_5 = m_4 + \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4-\lambda_5)\mu_1A}{N}$$

$$m_4 = m_3 + \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3-\lambda_4)\mu_1A}{N}$$

$$m_3 = m_2 + \frac{\lambda_4\lambda_5(\lambda_2+\mu_2-\lambda_3)\mu_1 A}{N}$$

Substituting the value of m_3, m_4 and m_5 in (C2), (C3) and (C4) respectively, we get,

$$\frac{dm_2}{dt} + (\lambda_2+\mu_2-\lambda_3)m_2 = \frac{\lambda_3\lambda_4\lambda_5(\lambda_2+\mu_2-\lambda_3)\mu_1 A}{N} \qquad (C29)$$

$$\frac{dm_3}{dt} + (\lambda_3+\mu_3-\lambda_4)m_3 = \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3-\lambda_4)\mu_1 A}{N} \qquad (C30)$$

$$\frac{dm_4}{dt} + (\lambda_4+\mu_4-\lambda_5)m_4 = \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4-\lambda_5)\mu_1 A}{N} \qquad (C31)$$

Similarly, in order to eliminate m_2, m_3 and m_4 from (C8) we find (m_2-m_5) from (C25) and (C22), (m_3-m_5) from (C25) and (C23) and (m_4-m_5) from (C25) and C24).

$$m_2 = m_5 + \frac{[\lambda_3\lambda_4\lambda_5-(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)]\mu_1 A}{N} \qquad (C32)$$

$$m_3 = m_5 + \frac{(\lambda_2+\mu_2)[\lambda_4\lambda_5-(\lambda_3+\mu_3)(\lambda_4+\mu_4)]\mu_1 A}{N} \qquad (C33)$$

$$m_4 = m_5 + \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_5-\lambda_4-\mu_4)\mu_1 A}{N} \qquad (C34)$$

Substituting the values of m_2, m_3 and m_4 in (C8), we find the following differential equation on simplification

$$\frac{dm_5}{dt} + (4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)m_5 = \frac{\mu_1 A(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)}{N}$$

To eliminate m_2 from (C1) we use the relation (C7) and substitute for m_5 and m_3 in terms of m_2 from (C32) and (C26) respectively. The value of m_4 can be obtained in terms of m_2 by substracting (C22) from (C24). Nonetheless, substituting the values of m_3, m_4 and m_5 in terms of m_2 in (C7) yields

$$m_2 = \frac{1}{4}[A-m_1-\{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)-\lambda_3\lambda_4\lambda_5+\lambda_5[(\lambda_2+\mu_2)(\lambda_3+\mu_3) -\lambda_4\lambda_3] +\lambda_4\lambda_5(\lambda_2+\mu_2-\lambda_3)\}\ \mu_1 A]$$

Substituting the value of m_2 in (C1) and simplifying we get

$$\frac{dm_1}{dt} + (\mu_1+\frac{\lambda_2}{4})m_1 = \frac{A}{4N}\ \lambda_2\lambda_5\lambda_4\lambda_3(4\mu_1+\lambda_2) \qquad \text{(C36)}$$

Thus we have succeeded in obtaining equations (C36), (C29) to (C31) and (C35) from equations (C1) to (C7). The equations obtained are linear differential equations of the first order and hence it is possible to give the complete solution explicitly. The complete solution of these linear differential equations can be written as

$$m_1(t) = e^{-(\mu_1+\frac{\lambda_2}{4})t}\ [\int \frac{\lambda_2 A}{4N}\ \lambda_5\lambda_4\lambda_3(4\mu_1+\lambda_2)\ e^{(\mu_1+\frac{\lambda_2}{4})t}\ dt+K_1] \qquad \text{(C37)}$$

$$m_2(t) = e^{-(\lambda_2+\mu_2-\lambda_3)t}\ [\int \frac{\lambda_3\lambda_4\lambda_5(\lambda_2+\mu_2-\lambda_3)\mu_1 A}{N}\ e^{(\lambda_2+\mu_2-\lambda_3)t}\ dt+K_2] \qquad \text{(C38)}$$

$$m_3(t) = e^{-(\lambda_3+\mu_3-\lambda_4)t}\ [\int \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3-\lambda_4)\mu_1 A}{N}\ e^{(\lambda_3+\mu_3-\lambda_4)t}\ dt+K_3] \qquad \text{(C39)}$$

$$m_4(t) = e^{-(\lambda_4+\mu_4-\lambda_5)t}\ [\int \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4-\lambda_5)\mu_1 A}{N}\ e^{(\lambda_4+\mu_4-\lambda_5)t}\ dt+K_4] \qquad \text{(C40)}$$

$$m_5(t) = e^{-(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)t}\ [\int \mu_1 \frac{A(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)}{N}\ \chi$$

$$e^{-(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)t}\ dt+K_5\ ] \qquad \text{(C41)}$$

where K_1, K_2, K_3, K_4 and K_5 are arbitrary constants. The value of these arbitrary constants can be determined from the initial conditions at t = 0. Thus integrating (C37) to (C41) and substituting (C6), we obtain the following solutions:

$$m_1(t) = \frac{\lambda_2\lambda_3\lambda_4\lambda_5 A}{N}\left[1-e^{-(\mu_1+\frac{\lambda_2}{4})t}\right] + a_1 e^{-(\mu_1+\frac{\lambda_2}{4})t}$$

$$m_2(t) = \frac{\lambda_3\lambda_4\lambda_5\mu_1 A}{N}\left[1-e^{-(\lambda_2+\mu_2-\lambda_3)t}\right] + a_2 e^{-(\lambda_2+\mu_2-\lambda_3)t}$$

$$m_3(t) = \frac{\lambda_4\lambda_5(\lambda_2+\mu_2)\mu_1 A}{N}\left[1-e^{-(\lambda_3+\mu_3-\lambda_4)t}\right] + a_3 e^{-(\lambda_3+\mu_3-\lambda_4)t}$$

$$m_4(t) = \frac{\lambda_5(\lambda_2+\mu_2)(\lambda_3+\mu_3)\mu_1 A}{N}\left[1-e^{-(\lambda_4+\mu_4-\lambda_5)t}\right] + a_4 e^{-(\lambda_4+\mu_4-\lambda_5)t}$$

$$m_5(t) = \frac{(\lambda_2+\mu_2)(\lambda_3+\mu_3)(\lambda_4+\mu_4)\mu_1 A}{N}\left[1-e^{-(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)t}\right] + a_5 e^{-(4\mu_1-\mu_2-\mu_3-\mu_4+\lambda_5)t}$$

APPENDIX IV

Case 1

L	N_R	$N(C_4)$	$N(C_3)$
1	1	4	0
2	4	8	0
3	9	12	0
4	16	16	0
4	25	20	0
Formula	L^2	4L	0

Case 2

L	N_R	$N(C_4)$	$N(C_3)$
1	36	24	0
2	140	40	4
3	312	56	8
4	552	72	12
Formula	2L(17L+1)	8(2L+1)	4(L-1)

Case 3

L	N_R	$N(C_4)$	$N(C_3)$
1	45	20	4
2	249	36	16
3	617	52	28
4	1149	68	40
Formula	$2(41L^2-21L)+5$	4(4L+1)	4(3L-2)

Case 4

L	N_R	$N(C_4)$	$N(C_3)$
1	32	16	4
2	120	24	12
3	264	32	20
4	464	40	28
Formula	$4L(7L+1)$	$8(L+1)$	$4(2L-1)$

Case 5

L	N_R	$N(C_4)$	$N(C_3)$
1	52	16	8
2	196	24	20
3	432	32	32
4	760	40	44
Formula	$2L(23L+3)$	$8(L+1)$	$4(3L-1)$

Case 6

L	N_R	$N(C_4)$	$N(C_3)$
1	5	4	4
2	13	4	8
3	25	4	12
4	41	4	16
Formula	$2L(L+1)+1$	4	$4L$

APPENDIX V

MONTE CARLO METHOD

The Monte Carlo Method, in general, is used to solve problems which depend in some important way upon probability; problems where physical experimentation is impracticable and the creation of an exact formula is impossible. Thus, the application of Monte Carlo Method is very essential to our problem.

During the simulation of the process, it is necessary to obtain simulated statistics of the process which is entirely numerical in nature and is carried out by supplying the pseudorandom numbers into the process or system under study and obtaining numbers (random variates) from it as answers.

The degree of success with which a computation may be made by the Monte Carlo Method on electronic computers is determined by the quality of the source of random numbers, which depends upon the choice of the method of generation of random numbers.

The uniformly-distributed random numbers which are required during the simulation can be obtained in various ways on a computer.

The first technique which is used comparatively rarely is to read a table of uniformly-distributed random numbers into the computer storage. The main disadvantage of this method in addition to the extra computer storage it takes is that for the solution of the problem for one set of input of overall probabilities, we frequently require $\sim 10^4$ random numbers, which is many times greater than the size of existing tables of uniformly-distributed random numbers.

The second technique for generating random numbers consists of using special apparatus on the computer -- a "random number device" which

transforms the results of some random physical process into random numbers. The register in which the random numbers are generated is usually assigned an address within the general system of addresses in the computer storage. Then a reference to the random number device reduces to a reading from that storedin the machine. The disadvantages of this method are (i) there is a risk of instability in random number devices and hence, they need periodic testing; (ii) it is impossible to reproduce exactly the results of the computation of a problem. Although this method increases the speed of a computation, for occasional use, the maintenance in working condition of random number device demands a considerable amount of work.

The last technique and the one we have used and which is being widely used is to find a random number, by means of a recurrence relation. Each successive number α_{j+1} is formed from a preceding number α_j by applying some algorithm consisting of arithmetic and logical operation. Such a sequence of numbers is not random but nevertheless, it may satisfy various statistical criteria of randomness. These numbers are thus called pseudo-random numbers. The main advantage of this method is the random numbers are reproducible and hence we can check their randomness. A subroutine was available for generating pseudo random numbers at the computer section of the McMaster University and it could be used on CDC-3600 computer. In this case, the first hundred numbers produced were destroyed in order to improve the randomness of the pseudo random numbers.

The aim is to use the random number generated at a particular instant to choose which characteristic site C_j should be removed from the surface of the crystal. As it is known that only one type of characteristic site can be removed at any discrete moment of time, then the events pertaining

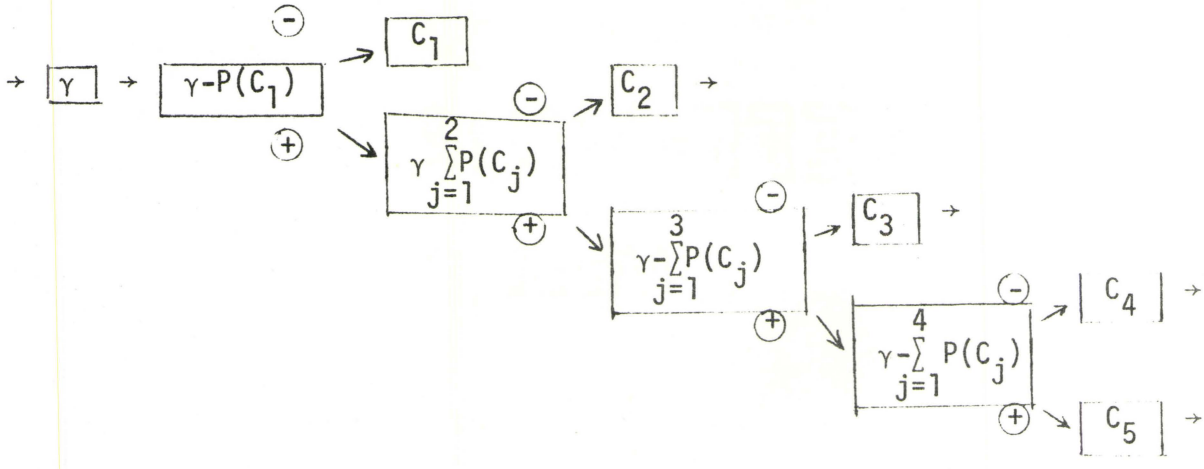
to the removal of a characteristic site C_j are mutually exclusive events with probabilities $P(C_1)$, $P(C_2)$, ... $P(C_5)$ respectively and

$$\sum_{j=1}^{5} P(C_j) = 1$$

then

$$P(C_1) + \ldots + P(C_{j-1}) \leq \gamma < P(C_1) + \ldots + P(C_j) \qquad j = 1,2,3,4,5$$

determines the type of the characteristic site (C_j) to be removed. γ is a uniformly-distributed pseudo random number. The following is the flow diagram which schematizes the procedure



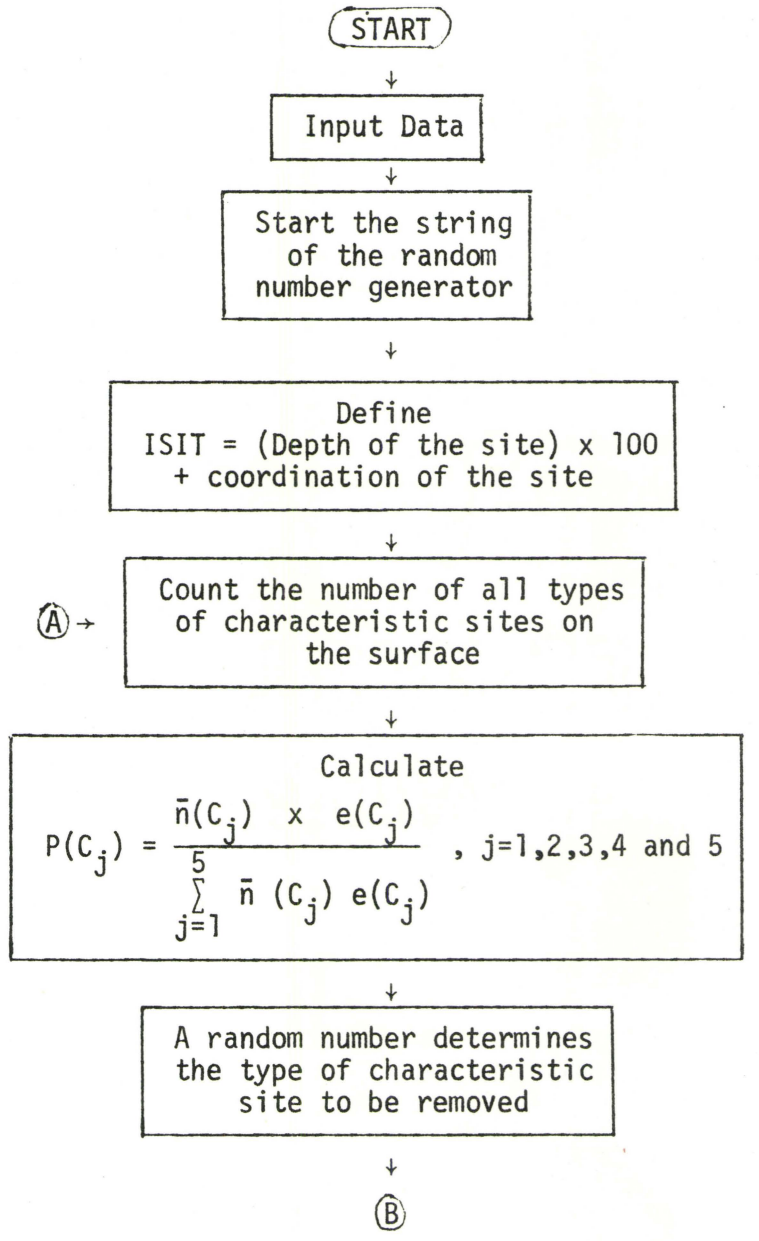
The box containing γ always denotes reference to the subroutine FRANDN generating the next random number of the sequence.

In the case when we have to choose one characteristic site for removal out of a set of a particular type of characteristic sites, the procedure is still shorter. Here, we multiply the random number generated with the total number $\bar{n}(C_j)$ of that particular type of characteristic site at that instant. The resulting number gives the location of the atom site to be removed, i.e.

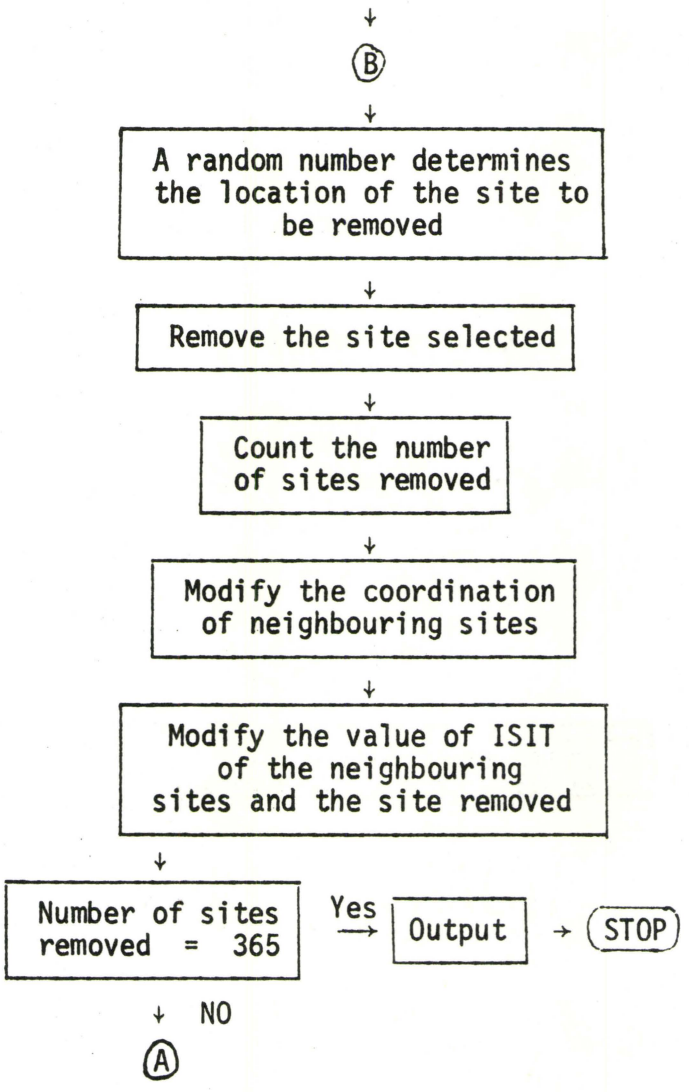
location of atom site to be removed = $\gamma * \bar{n}(C_j)$ $\qquad j = 1,2,3,4$ and 5 .

APPENDIX VI

FLOWCHART



continued .....


B
A random number determines the location of the site to be removed
Remove the site selected
Count the number of sites removed
Modify the coordination of neighbouring sites
Modify the value of ISIT of the neighbouring sites and the site removed
Number of sites removed = 365
Yes
Output
STOP
NO
A

APPENDIX VII
COMPUTER PROGRAMME

```
      PROGRAM EVAP(INPUT=1003,OUTPUT=1003)
      COMMON ISIT(16900)
      READ 1000,M,NSETS
      DO 10 N=1,NSETS
      CALL SECOND(TLAST)
      IT=TLAST*1000.+1.
      CALL FRANDM(ISIT,100,IT)
      CALL WORK(ISIT,M)
      CALL SECOND(TNOW)
      T=TNOW-TLAST
      PRINT 2000,N,T,IT
   10 CONTINUE
      STOP
 1000 FORMAT(2I5)
 2000 FORMAT(*0TIME IN SECONDS FOR SET*,I3,* WAS*,F8.3,5X,*STARTING INTE
     $GER FOR RANDOM NUMBER GENERATOR WAS*,I10)
      END



      SUBROUTINE WORK(ISITE,M)
      COMMON ISIT(10000)
      COMMON/NAME/NR(5),NS(5),NMAKE(5),NKILL(5)
      DIMENSION ISITE(M,M),IST(100),P(5),X(5)
      DIMENSION SPROB(5),Y(5)
      MM=M*M
      JREM=0
      NS(1)=NS(2)=NS(3)=NS(4)=0
      DO 14 I=1,5
   14 SPROB(I)=0.0
      DO 5 I=1,MM
    5 ISIT(I)=100
      NS(5)=MM
      READ 1000,N,JMAX
 1000 FORMAT(14I5)
      PRINT 2000,N
 2000 FORMAT(*1NUMBER OF SITES REMOVED INITIALLY*,I5)
      DO 1000 I,J
      N=N-1
      IJ=I+(J-1)*M
      CALL REMOVE(IJ,M)
      IF(N .GT.0) GO TO 10
      DO 15 I=1,5
   15 NR(I)=NMAKE(I)=NKILL(I)=0
      READ 1100,P
 1100 FORMAT(5F14.11)
      SP=0.0
      DO 300 I=1,5
  300 SP=SP+P(I)
      DO 400 I=1,5
  400 Y(I)=P(I)/SP
      XX=Y(1)/Y(3)
```

```
      XY=Y(2)/Y(3)
      XZ=Y(4)/Y(3)
      XO=Y(5)/Y(3)
      PRINT 1200,P
  200 FORMAT(*0PROBABILITIES OF REMOVING CO-ORDINATION NUMBERS 1 TO 5 AR
     $E*,3X,5E14.5)
      PRINT 1400,Y
  400 FORMAT(*0THE VALUES OF P(I)/(SUM OF ALL P(I)) WITH I VARYING FROM
     $1 TO 5 ARE*,3X,5E12.5)
      PRINT 1300,XX,XY,XZ,XO
  300 FORMAT(*0PROPENSITIES WITH RESPECT TO KINK SITES ARE*,3X,4E14.5)
      PRINT 3000
 3000 FORMAT(1H1,///,27X,*INITIAL SURFACE*//)
      DO 30 J=1,M
      DO 20 I=1,M
   20 IST(I)=ISITE(I,J)/100
      PRINT 4000, (IST(I),I=1,M)
 4000 FORMAT(11X,120I1)
C     CALCULATE INSTANTANEOUS PROBABILITIES
   30 S=0.
      DO 40 I=1,5
   40 S=S+P(I)*NS(I)
      DO 50 I=1,5
      X(I)=P(I)*NS(I)/S
   50 SPROB(I)=SPROB(I)+X(I)
      CALL FRANDN(R,1,0)
      IF(R.LE.X(1)) GO TO 60
      X(2)=X(1)+X(2)
      IF(R.LE.X(2)) GO TO 70
      X(3)=X(2)+X(3)
      IF(R.LE.X(3)) GO TO 80
      X(4)=X(3)+X(4)
      IF(R.LE.X(4)) GO TO 90
      NC=5   $  GO TO 100
   60 NC=1   $  GO TO 100
   70 NC=2   $  GO TO 100
   80 NC=3   $  GO TO 100
   90 NC=4   $  GO TO 100
  100 CALL FRANDN(R,1,0)
      IR=R*NS(NC)+1.
      MN=MM/2
      DO 120 IJ=1,MN
      IF(MOD(ISIT(1+MN-IJ),100).EQ.NC) IR=IR-1
      IF(IR) 130,130,110
  110 IF(MOD(ISIT(MN+IJ),100).EQ.NC) IR=IR-1
      IF(IR) 140,140,120
  120 CONTINUE
  130 IJ=MM   $  GO TO 150
  140 IJ=1+MN-IJ   $  GO TO 150
  150 IJ=IJ+MN
      CALL REMOVL(IJ,M)
      JREM=JREM+1
      IF(JREM.EQ.50)GO TO 180
      IF(JREM.EQ.100)GO TO 180
      IF(JREM.EQ.150)GO TO 180
      IF(JREM.EQ.200)GO TO 180
      IF(JREM.EQ.250)GO TO 180
      IF(JREM.EQ.275)GO TO 180
      IF(JREM.EQ.300)GO TO 180
      IF(JREM.EQ.325)GO TO 180
      IF(JREM.EQ.350)GO TO 180
```

```
      IF(JREM.LT.JMAX) GO TO 35
      DO 160 I=1,MM
  160 ISIT(I)=ISIT(I)/100
      PRINT 5000,NR,JREM
 5000 FORMAT(*0NUMBER OF SITES REMOVED WITH CO-ORDINATION NUMBERS 1 TO 5
     $ ARE*,5I5,3X,*TOTAL NUMBER REMOVED WAS*,I5)
      PRINT 7000,NMAKE
      PRINT 8000,NKILL
 8000 FORMAT(*0NUMBER OF SITES CREATED WITH CO-ORDINATION NUMBERS 1 TO 5
     $ ARE*,5I5)
 7000 FORMAT(*0NUMBER OF SITES DESTROYED WITH CO-ORDINATION NUMBERS 1 TO
     $ 5 ARE*,5I5)
      PRINT 6000,NS
 6000 FORMAT(*0NUMBER OF REMAINING SITES WITH CO-ORDINATION NUMBERS 1 TO
     $ 5 ARE*,5I5)
      PRINT 7500,SPROB
 7500 FORMAT(*0SUM OF INSTANTANEOUS PROBABILITIES FOR TOTAL REMOVAL IS*,
     $5F14.5//)
      IF(JREM.LT.JMAX) GO TO 35
      PRINT 8500
 8500 FORMAT(1H1,///,17X,*SURFACE AFTER REMOVAL OF 365 SITES*//)
      DO 170 J=1,M
  170 PRINT 4000, (ISITE(I,J),I=1,M)
   35 RETURN
      END



      SUBROUTINE REMOVE(IJ,M)
      COMMON ISIT(16900)
      COMMON/NAME/NR(5),NS(5),NMAKE(5),NKILL(5)
      N=ISIT(IJ)
      NC=MOD(N,100)
      IL=N/100
      NS(NC)=NS(NC)-1
      NR(NC)=NR(NC)+1
      NKILL(NC)=NKILL(NC)+1
      ILN=(IL+1)*100+6
      NC=-1
      NN=ISIT(IJ+1)
      IF(NN.GE.ILN) NC=NC-1
      IF(NN/100.NE.IL) GO TO 10
      NCN=MOD(NN,100)
      NS(NCN)=NS(NCN)-1
      NKILL(NCN)=NKILL(NCN)+1
      NS(NCN-1)=NS(NCN-1)+1
      NMAKE(NCN-1)=NMAKE(NCN-1)+1
      ISIT(IJ+1)=NN-1
   10 NN=ISIT(IJ-1)
      IF(NN.GE.ILN) NC=NC-1
      IF(NN/100.NE.IL) GO TO 20
      NCN=MOD(NN,100)
      NS(NCN)=NS(NCN)-1
      NKILL(NCN)=NKILL(NCN)+1
      NS(NCN-1)=NS(NCN-1)+1
      NMAKE(NCN-1)=NMAKE(NCN-1)+1
      ISIT(IJ-1)=NN-1
   20 NN=ISIT(IJ+M)
      IF(NN.GE.ILN) NC=NC-1
      IF(NN/100.NE.IL) GO TO 30
      NCN=MOD(NN,100)
```

```
      NS(NCN)=NS(NCN)-1
      NKILL(NCN)=NKILL(NCN)+1
      NS(NCN-1)=NS(NCN-1)+1
      NMAKE(NCN-1)=NMAKE(NCN-1)+1
      ISIT(IJ+M)=NN-1
   4  NN=ISIT(IJ-M)
      IF(NN.GE.ILN) NC=NC-1
      IF(NN/100.NE.IL) GO TO 40
      NCN=MOD(NN,100)
      NS(NCN)=NS(NCN)-1
      NKILL(NCN)=NKILL(NCN)+1
      NS(NCN-1)=NS(NCN-1)+1
      NMAKE(NCN-1)=NMAKE(NCN-1)+1
      ISIT(IJ-M)=NN-1
   3  ISIT(IJ)=ILN+NC
      NS(6+NC)=NS(6+NC)+1
      NMAKE(6+NC)=NMAKE(6+NC)+1
      RETURN
      END
```

Table 1

Definition of Characteristic Sites for
Simple Cubic Crystal

Surface atom	Number of First Neighbours(j)	Notation used for the atom site	
In-terrace	5	C_5	5
In-ledge	4	C_4	4
Kink	3	C_3	3
At-Ledge	2	C_2	2
Ad-atom	1	C_1	1

Table 2

Behaviour of $\frac{m_4}{m_3}$ when $a_3 = 0$ and $a_4 = 0$ *

Condition for X_4 and X_3	$\frac{m_4}{m_3}$
$X_4 = 0$ and $X_3 > 0$	zero
$X_4 > 0$ and $X_3 = 0$	infinite
$X_4 > 0$ and $X_3 > 0$	finite and constant

* Applicable for short times

Table 3

Behaviour of $m_4(t)/m_3(t)$ and Q
with Different Surface Conditions *

	Surface Condition	$\frac{m_4(t)}{m_3(t)}$	Q
$> L_3$ and $a_4 > L_4$	(i) $X_3 < 0$ and $X_4 < 0$	constant	finite and constant
	(ii) $X_3 < 0$ and $X_4 \geq 0$	tends to zero	zero
	(iii) $X_3 \geq 0$ and $X_4 < 0$	tends to infinite	infinite
$< L_3$ and $a_4 > L_4$	(i)* $X_3 > 0$ and $X_4 = 0$	tends to constant	--
	(ii) $X_3 > 0$ and $X_4 > 0$	tends to constant	condition for dynamic equilibrium
	(iii)* $X_3 = 0$ and $X_4 > 0$	tends to constant	--
	(iv) $X_3 \geq 0$ and $X_4 < 0$	tends to infinite	infinite
$> L_3$ and $a_4 < L_4$	(i) $X_3 > 0$ and $X_4 > 0$	tends to constant	condition for dynamic equilibrium
	(ii)* $X_3 = 0$ and $X_4 > 0$	tends to constant	--
	(iii)* $X_3 > 0$ and $X_4 = 0$	tends to constant	--
	(iv) $X_3 < 0$ and $X_4 \geq 0$	tends to zero	zero
$< L_3$ and $a_4 < L_4$	(i) $X_3 > 0$ and $X_4 > 0$	tends to constant	condition for dynamic equilibrium
	(ii)* $X_3 = 0$ and $X_4 > 0$		--
	(iii)* $X_3 > 0$ and $X_4 = 0$		--
L_3 and $a_4 = L_4$	$X_3 \gtrless 0$ and $X_4 \gtrless 0$	constant at t = 0	dynamic equilibrium
L_3 and $a_4 > L_4$	(i) $X_3 \gtrless 0$ and $X_4 > 0$	tends to constant	condition for dynamic equilibrium
	(ii) $X_3 \gtrless 0$ and $X_4 < 0$	tends to infinite	infinite
L_3 and $a_4 = L_4$	(i) $X_3 > 0$ and $X_4 \gtrless 0$	tends to constant	condition for dynamic equilibrium
	(ii) $X_3 < 0$ and $X_4 \gtrless 0$	tends to zero	zero
L_3 and $a_4 < L_4$	$X_3 \gtrless 0$ and $X_4 > 0$	tends to constant	condition for dynamic equilibrium
L_3 and $a_4 = L_4$	$X_3 > 0$ and $X_4 \gtrless 0$	tends to constant	condition for dynamic equilibrium

* Applicable for short times

Table 4

Behaviour of $N(C_3)$, $N(C_4)$ and $N(C_4)/N(C_3)$ for Different Step Systems*

Step System	Number of Kink Sites	Number of in-ledge sites	$\frac{N(C_4)}{N(C_3)}$
00)[010]	(i) zero	(i) increases with time	(i) infinite
	(ii) finite and constant with time	(ii) increases with time	(ii) increases with time (tends to infinite at large times)
00)[011] and 00)[010]	increases with time	increases with time	constant at large times
00)[011]	increases with time	constant with time	decreases with time (tends to zero at large times)

* Applicable for short times

Table 5

$\bar{K}$ For Different Step Systems

Case Number	Step System	$\bar{K}$
1	(100)[010]	zero
2	(100)[011] and (100)[010]	4.0
3	(100)[011] and (100)[010]	1.333
4	(100)[011] and (100)[010]	1.0
5	(100)[011] and (100)[010]	0.6666
6	(100)[011]	infinite

Table 6

Conditions for Obtaining Pit Shapes *

Step System	Condition
(100)[010]	$a_3 > L_3$ and $a_4 > L_4$ $\quad X_3 \geq 0$ and $X_4 < 0$
	$a_3 < L_3$ and $a_4 > L_4$
	$a_3 = L_3$ and $a_4 > L_4$, $X_3 \gtrless 0$ and $X_4 < 0$
(100)[011]	$a_3 > L_3$ and $a_4 > L_4$ $\quad X_3 < 0$ and $X_4 \geq 0$
	$a_3 > L_3$ and $a_4 < L_4$
	$a_3 > L_3$ and $a_4 = L_4$, $X_3 < 0$ and $X_4 \gtrless 0$
(100)[010] and (100)[011]	$a_3 > L_3$ and $a_4 > L_4$, $X_3 < 0$ and $X_4 < 0$

* Applicable for short times

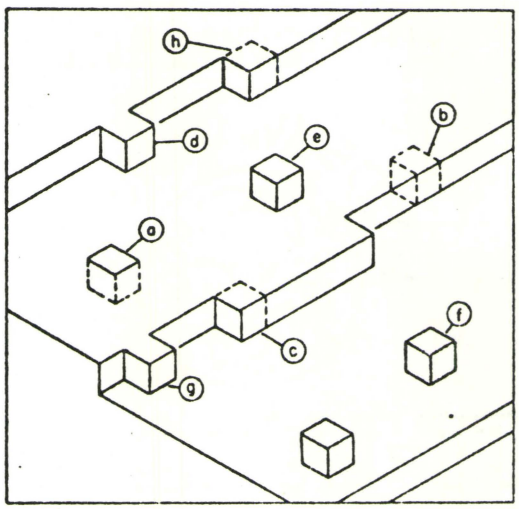
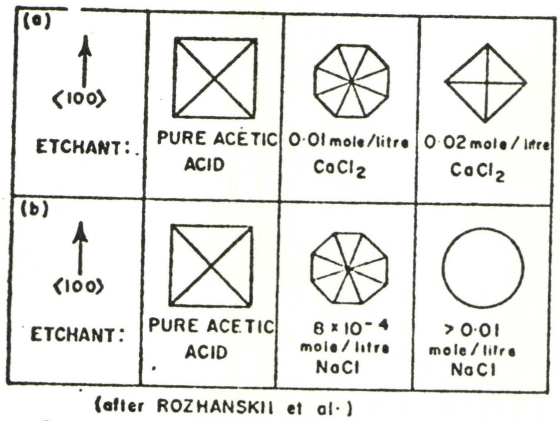


***Fig. 1.**.Schematic view of metal-vapor interface, depicting ledges and atoms in sites* (a) *in surface,* (b) *in ledge,* (c) *kink,* (d) *at ledge, and* (e) *adsorbed on the surface, and impurity atoms* (f) *adsorbed,* (g) *at ledge, and* (h) *"poisoning" a kink*



(after ROZHANSKII et al.)

Figure 2 - Summary of studies on the etching of sodium chloride in acetic acid-based solvents (after Rozhanskii *et al.*).

ETCHING CONDITIONS	OPTIMUM CONCENTRATIONS		
	$CdCl_2$ 2×10^{-4} MOLAR PARTS	$CdBr_2$ $3{\cdot}3 \times 10^{-3}$ MOLAR PARTS	CdI_2 $9{\cdot}4 \times 10^{-3}$ MOLAR PARTS
SHORT ETCHING TIME OR LOW TEMPERATURE	[100] [010]		
QUIESCENT ETCHING FOR OVER TWO MINUTES			
ETCHING WITH STIRRING			
ETCHING AT ELEVATED TEMPERATURES T=50°C			

(after KOSTIN et al.)

Figure 3 - Summary of studies on the etching of sodium chloride in ethyl alcohol-based etchants (after KOSTIN *et al.*).

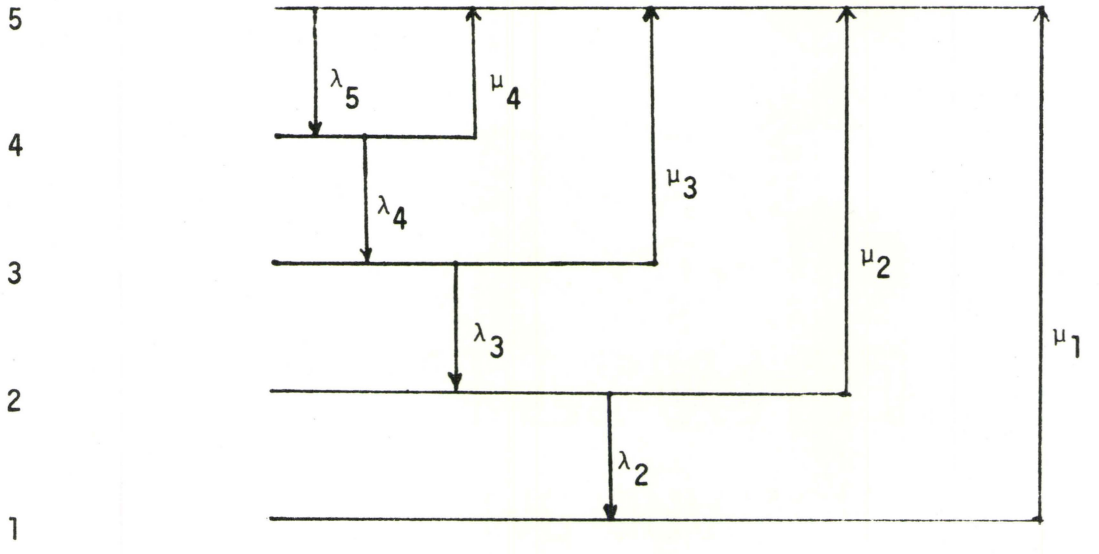


Figure 4

The Model

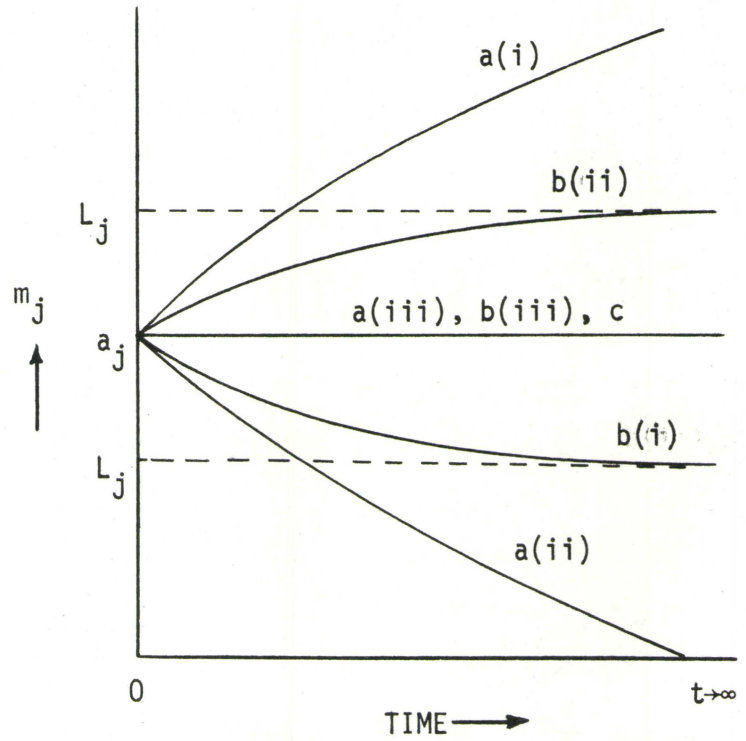


Fig. 5 Schematic behaviour of the mean value of the jth characteristic site with time when $a_j \neq 0$ and $L_j \neq 0$.

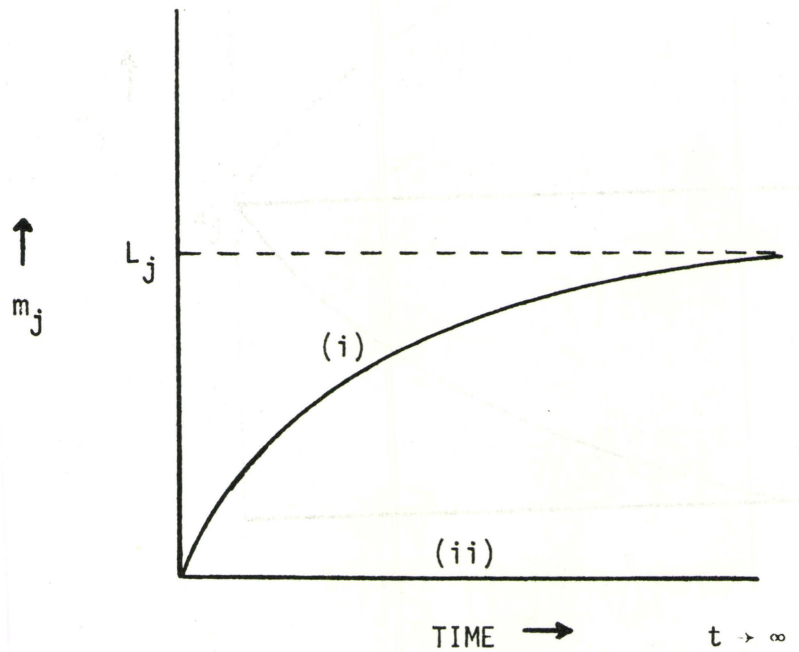


Fig. 6 Schematic behaviour of the mean value of the jth characteristic site with time when $a_j = 0$.

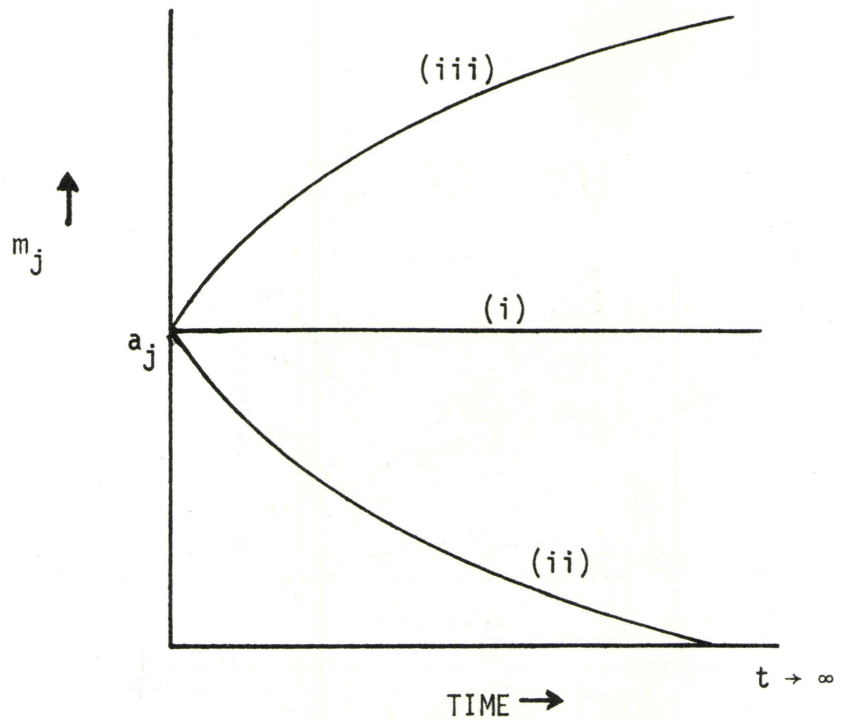


Fig. 7 Schematic behaviour of the mean value of the jth characteristic site with time when $L_j = 0$.

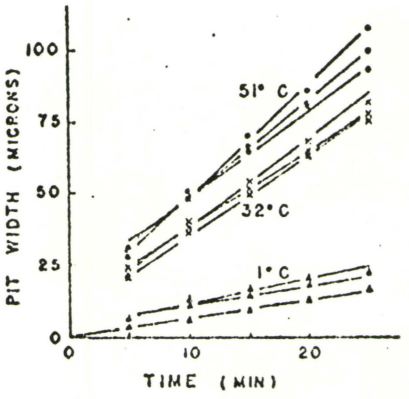


FIG. 8 Mean pit width as a function of total etching time in "W_P" etchant for the three temperatures shown.

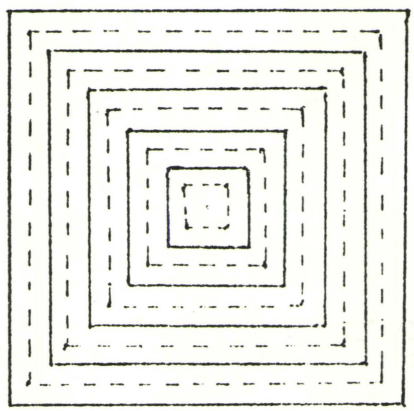


Figure 9. Case 1: (100)[010] in simple cubic
--- - Line joining the centres of the atoms removed.

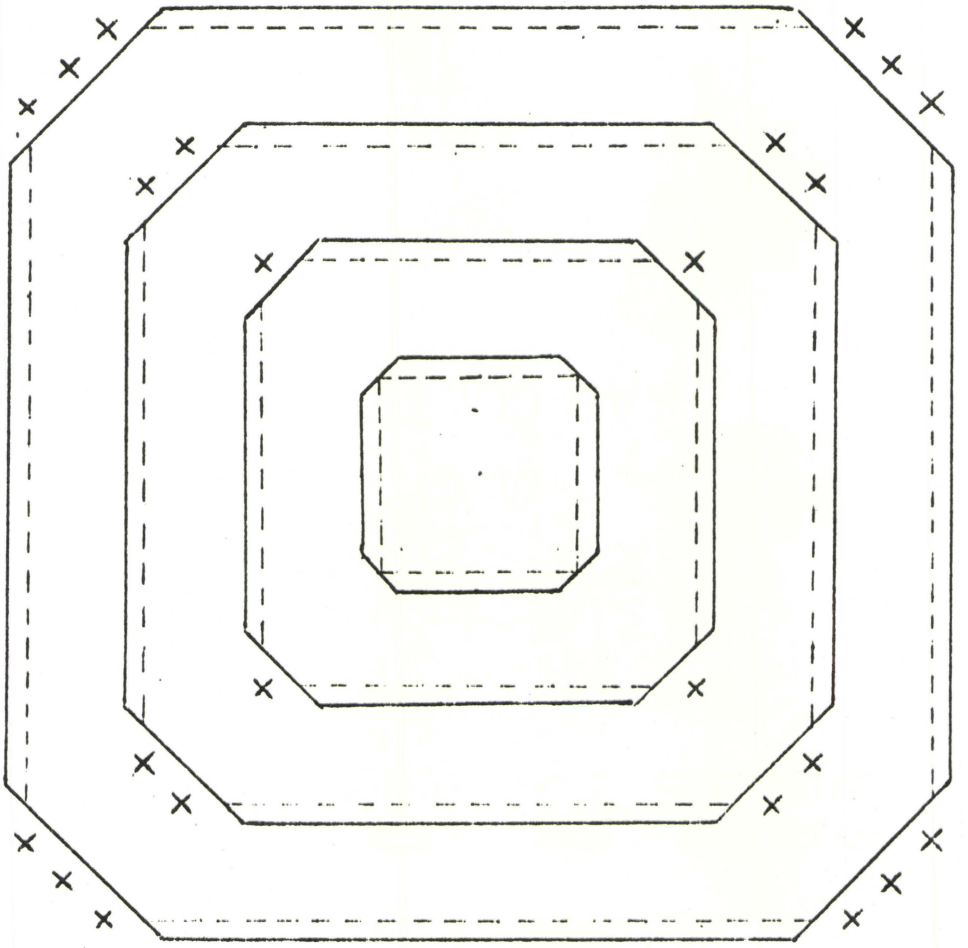


Figure 10. Case 2: (100)[011] and (100)[010] in simple cubic
x - kink atom; ---- - line joining the centres of the atoms removed.

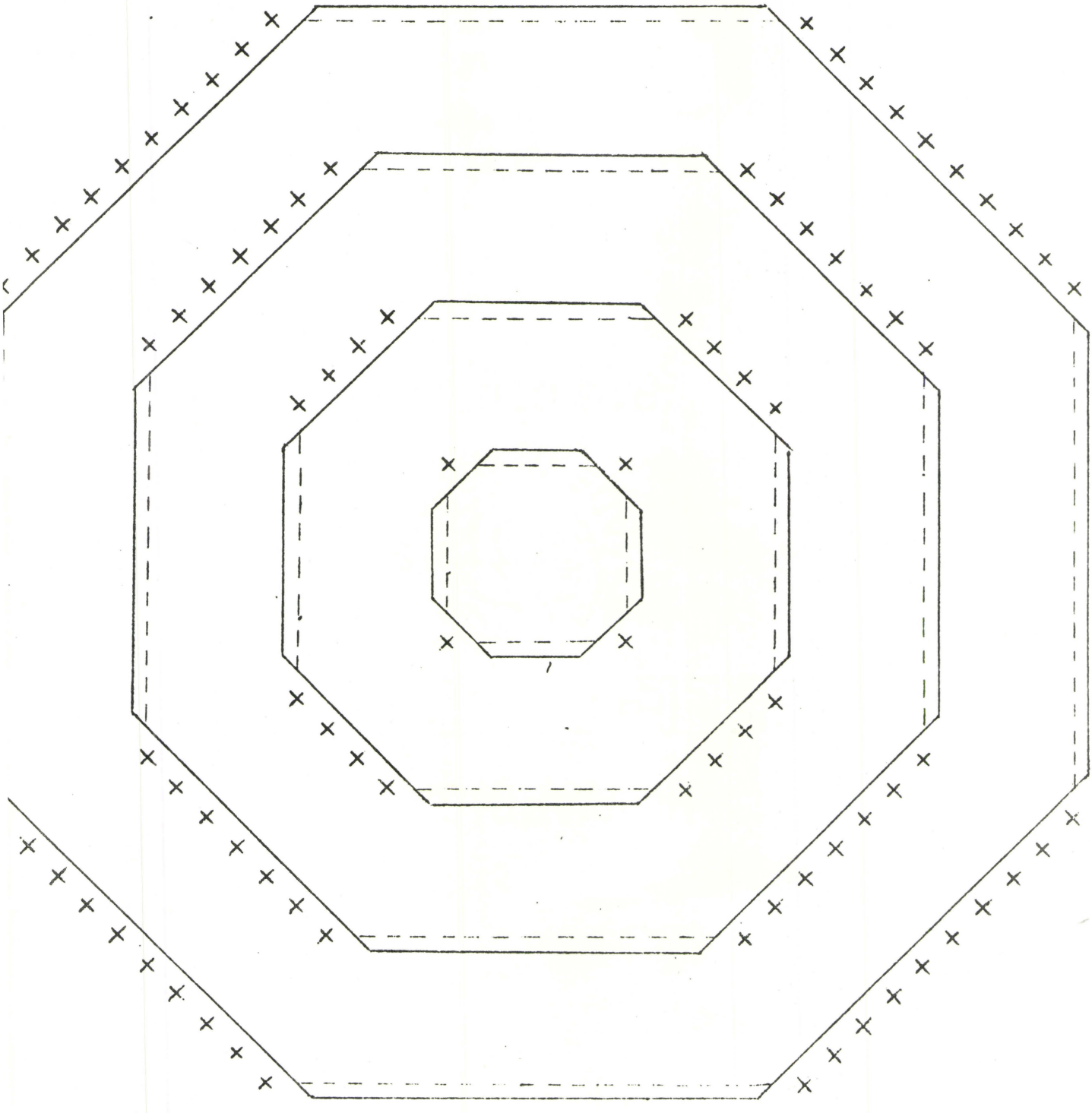


Figure 11. Case 3: (100)[011] and (100)[010] in simple cubic
x - kink atom; ---- - line joining the centres of the atoms removed.

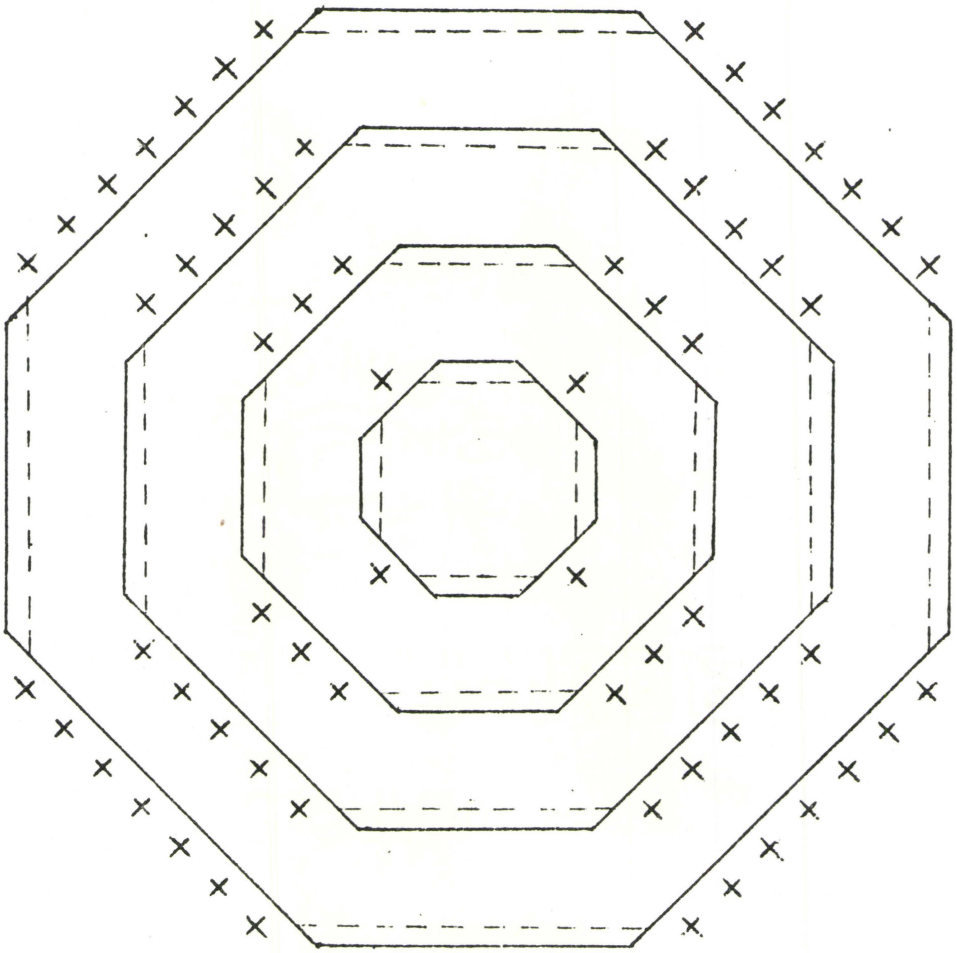


Figure 12. Case 4: (100)[011] and (100)[010] in simple cubic
x - kink atoms; ----- - line joining centres of atoms removed.

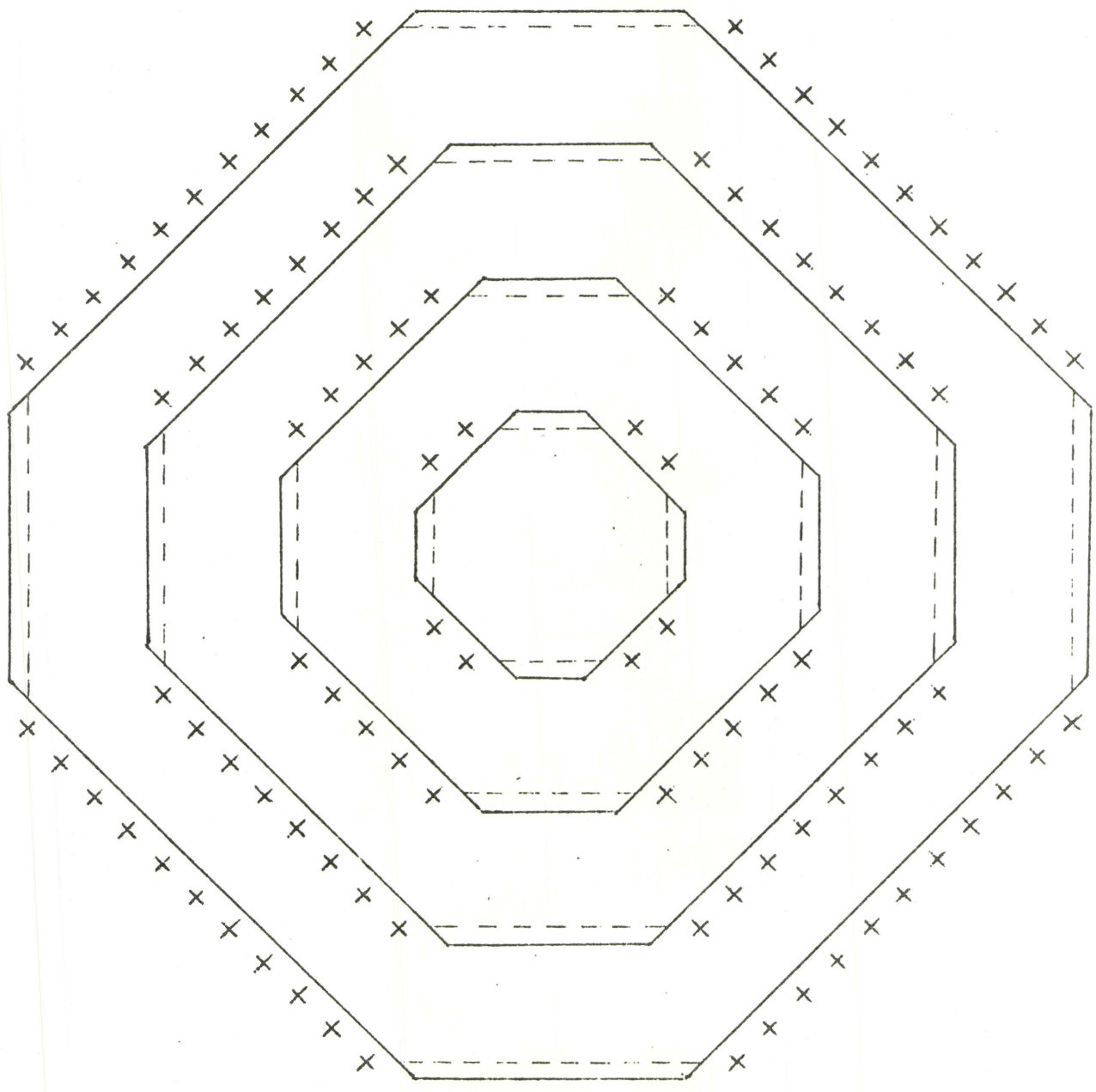


Figure 13. Case 5: (100)[011] and (100)[010] in simple cubic.
x - kink atom; ----- - line joining the centres of the atoms removed.

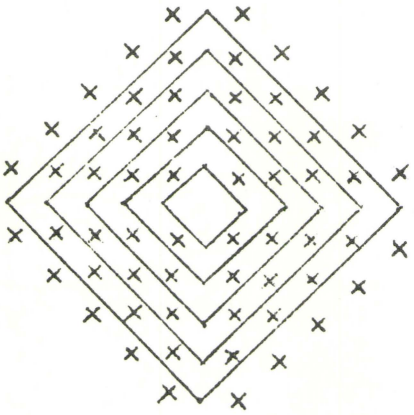


Figure 14. Case 6: (100)[011] in simple cubic
x - kink atom.

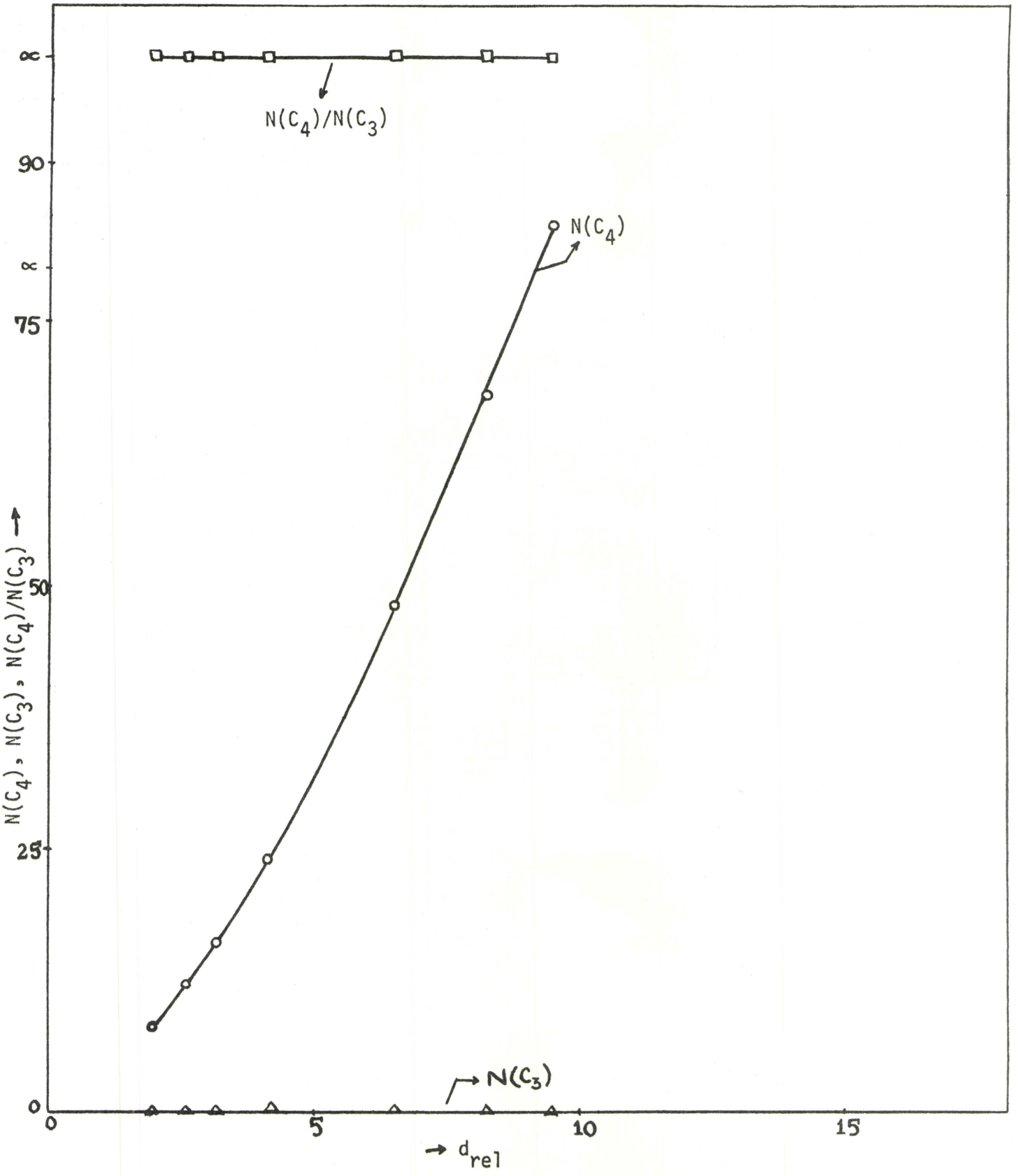


Fig. 15 Statistics of surface atoms for case 1, (100)[010] step system.

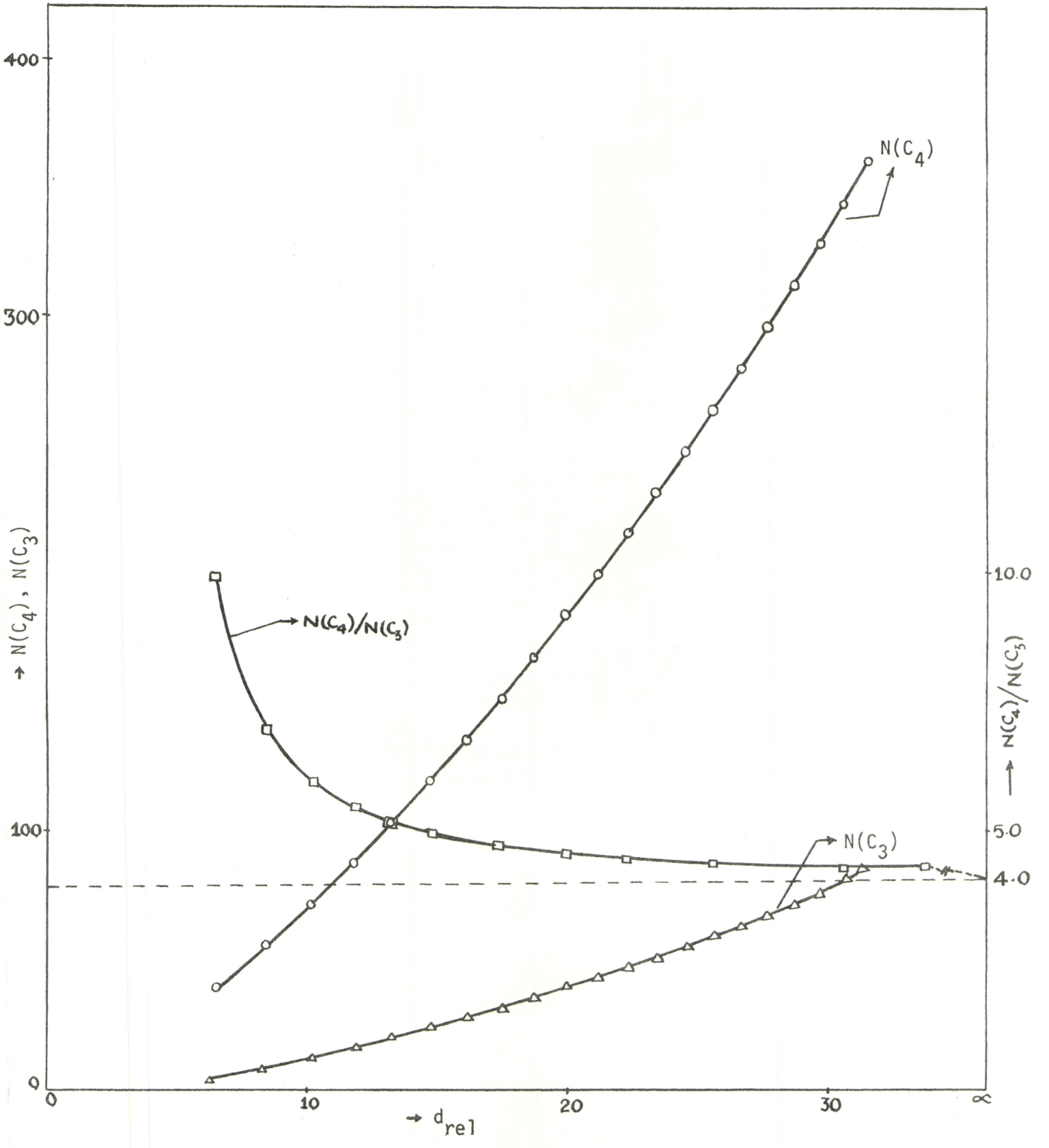


Fig. 16 Statistics of surface atoms for case 2, (100)[011] and (100)[010] step system.

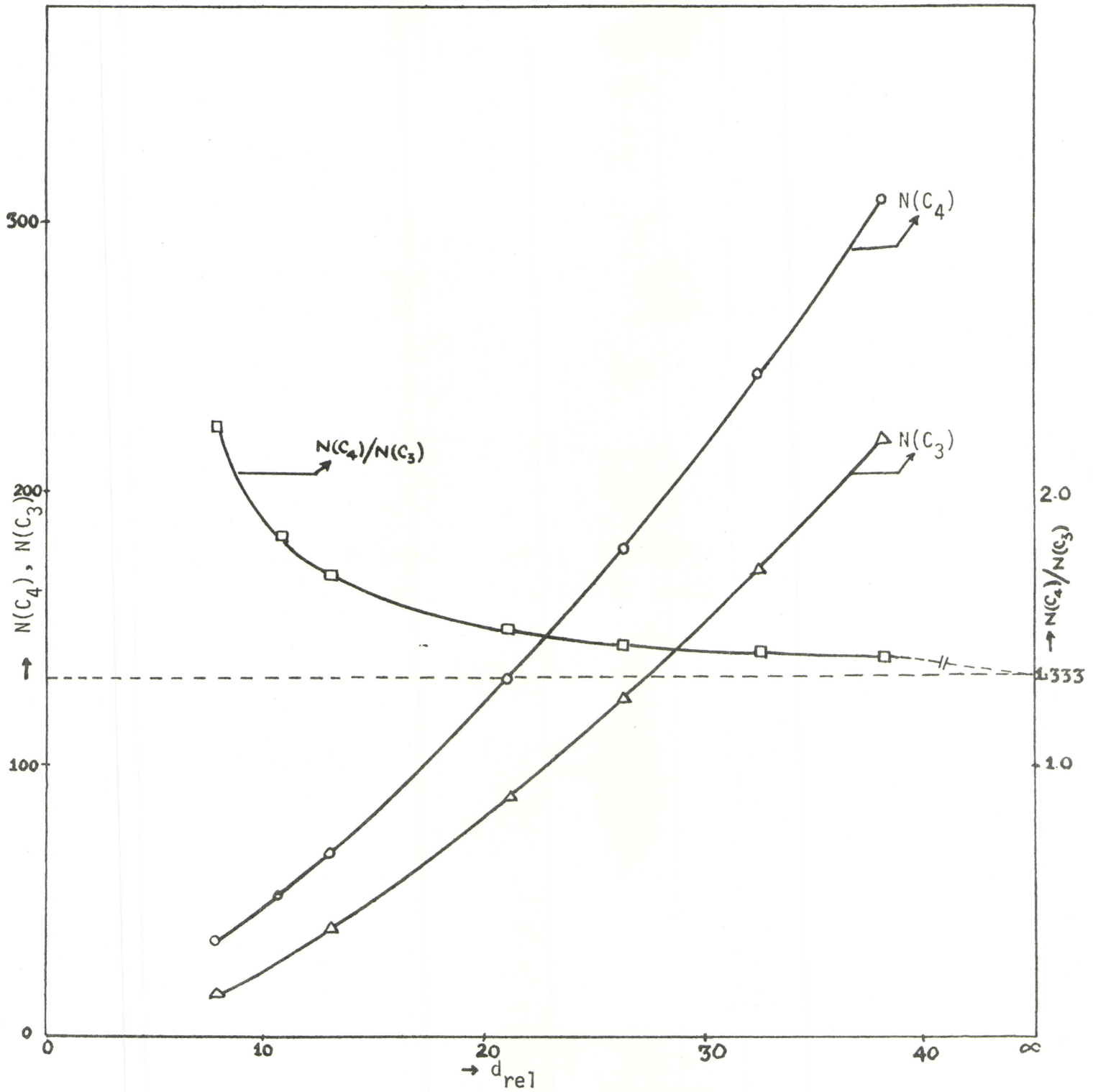


Fig. 17 Statistics of surface atoms for case 3, (100)[011] and (100)[010] step system.

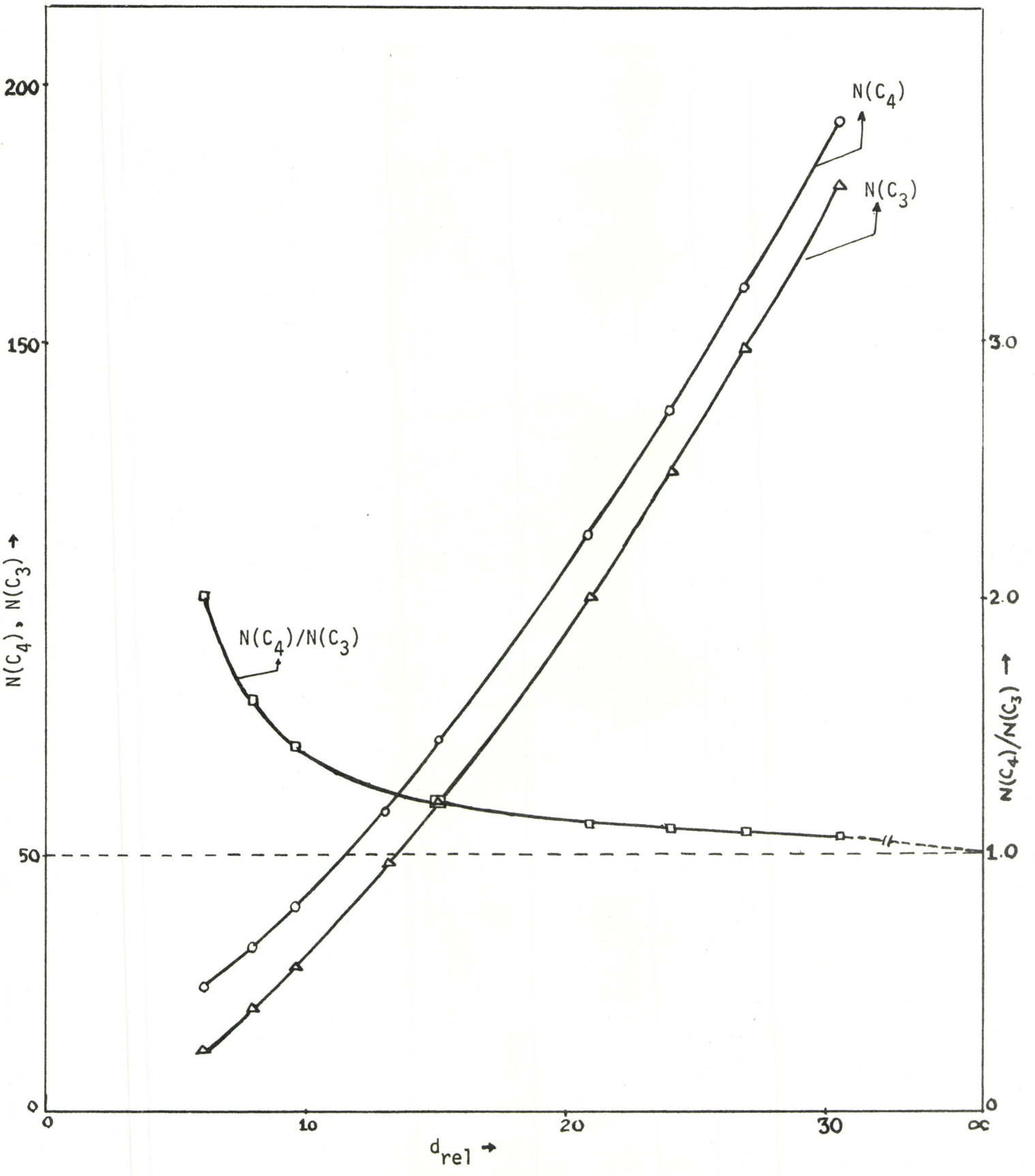


Fig. 18 Statistics of surface atoms for case 4, (100)[011] and (100)[010] step system.

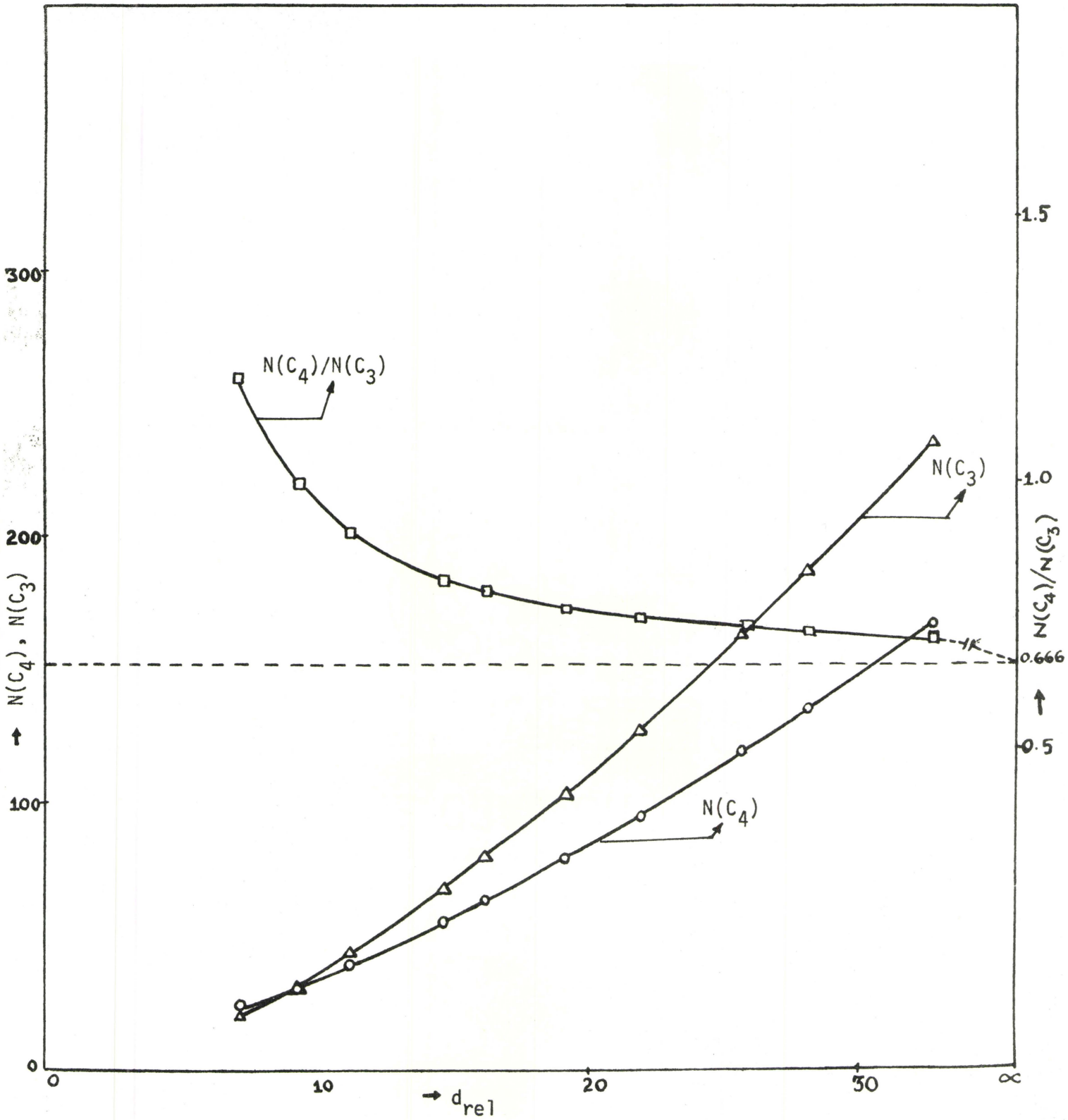


Fig. 19 Statistics of Surface atoms for case 5, (100)[011] and (100)[010] step system.

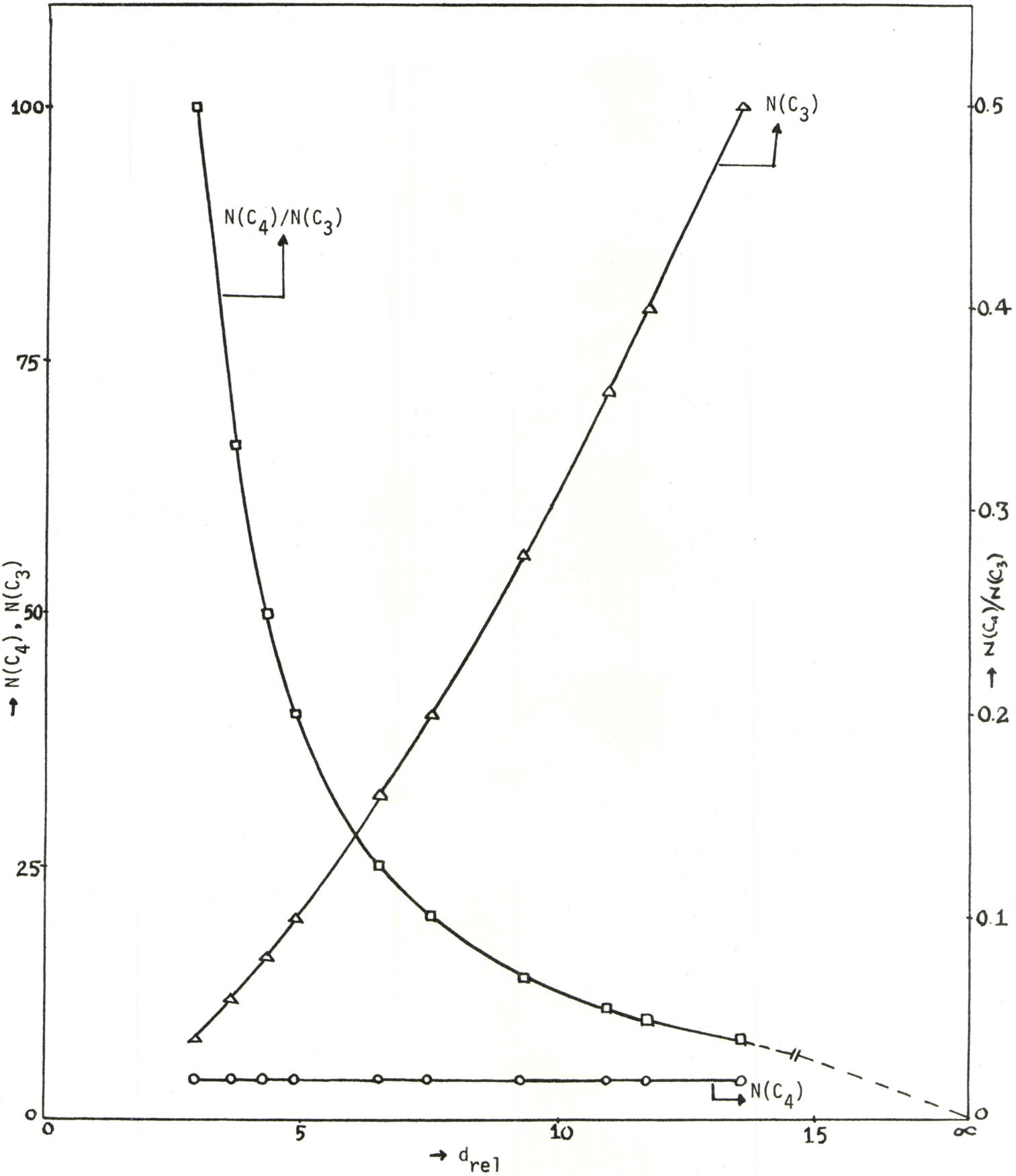


Fig. 20 Statistics of surface atoms for case 6, (100)[011] and (100)[010] step system.

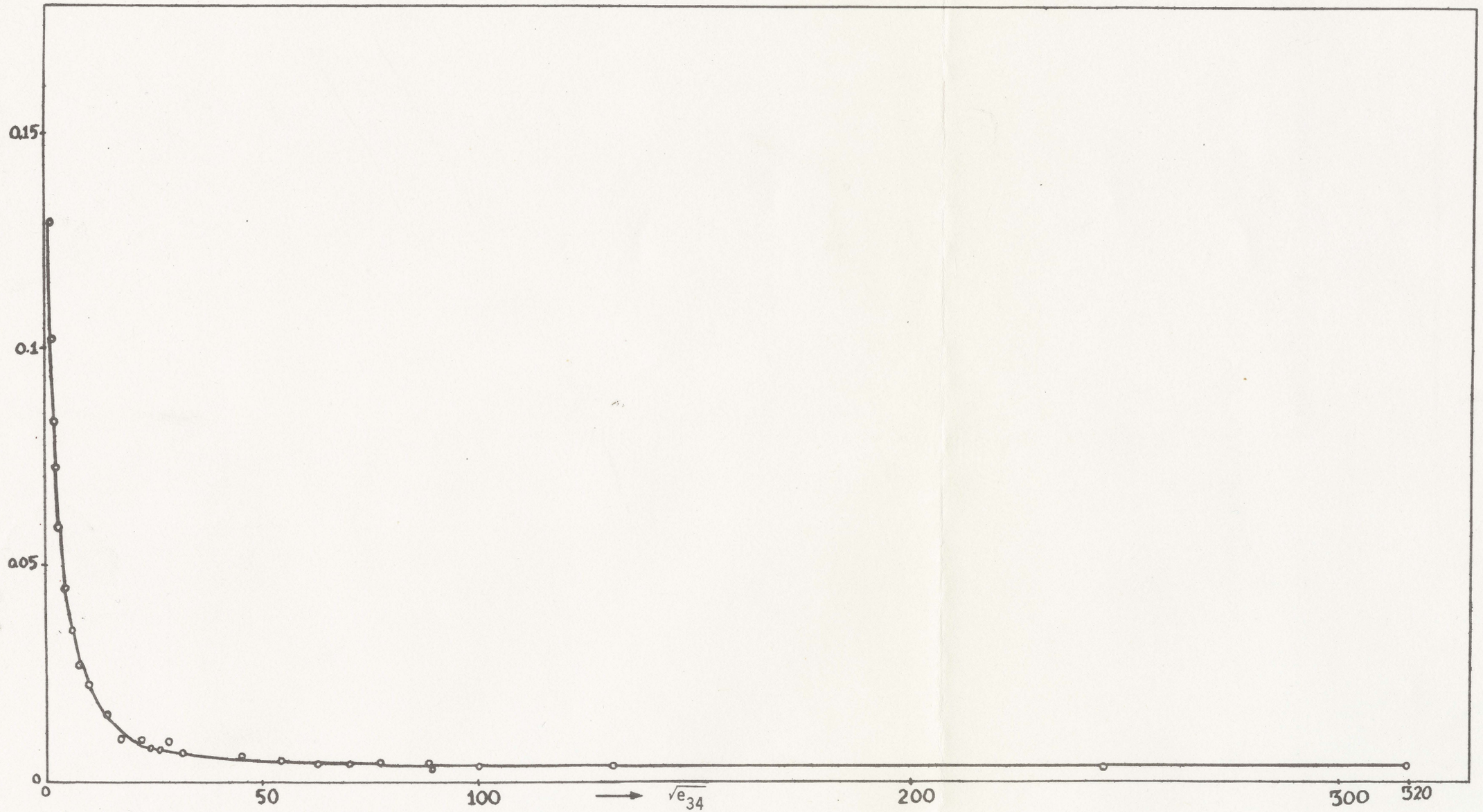


Fig. 21 Variation of population mean of kink sites on the surface with the square root of e_{34}

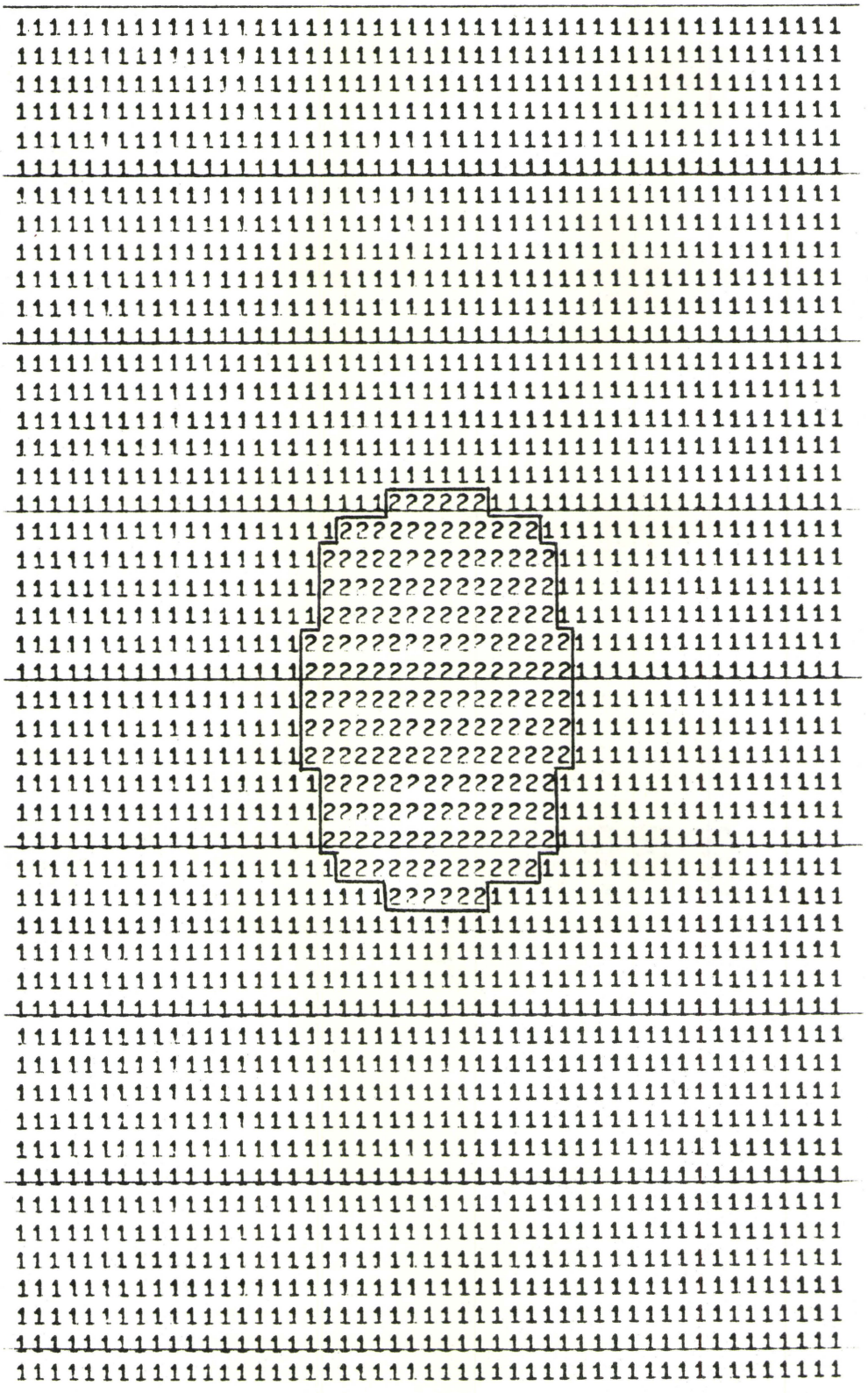


Figure 22(a). Initial distribution of sites on the surface.

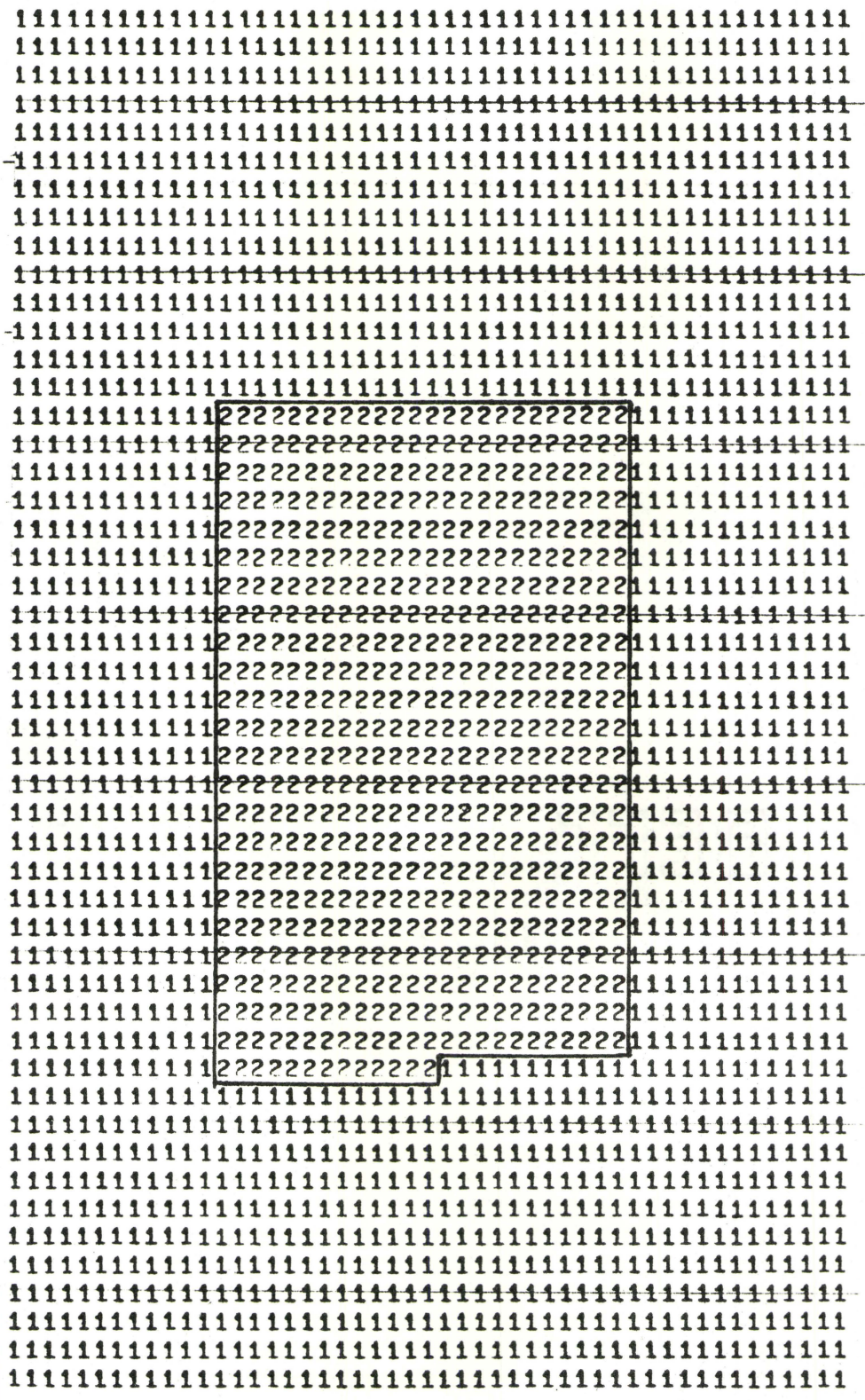


Figure 22(b). Distribution of sites on the surface after 365 removals for the overall probability of kink sites of 0.01.

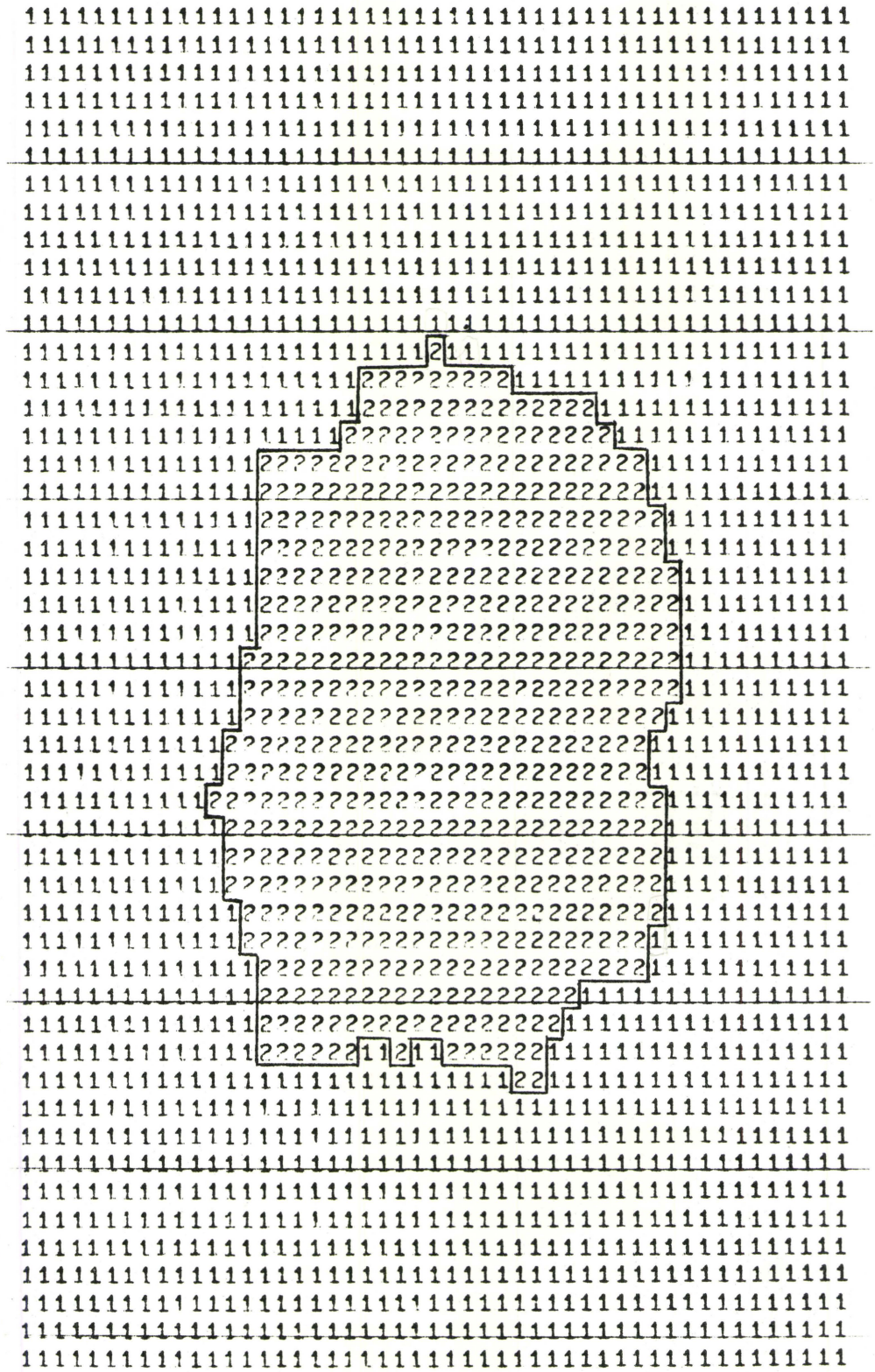


Figure 22 (c). Distribution of sites on the surface after 365 removals for the overall probability of kink sites of 1 x 10^{-4}.

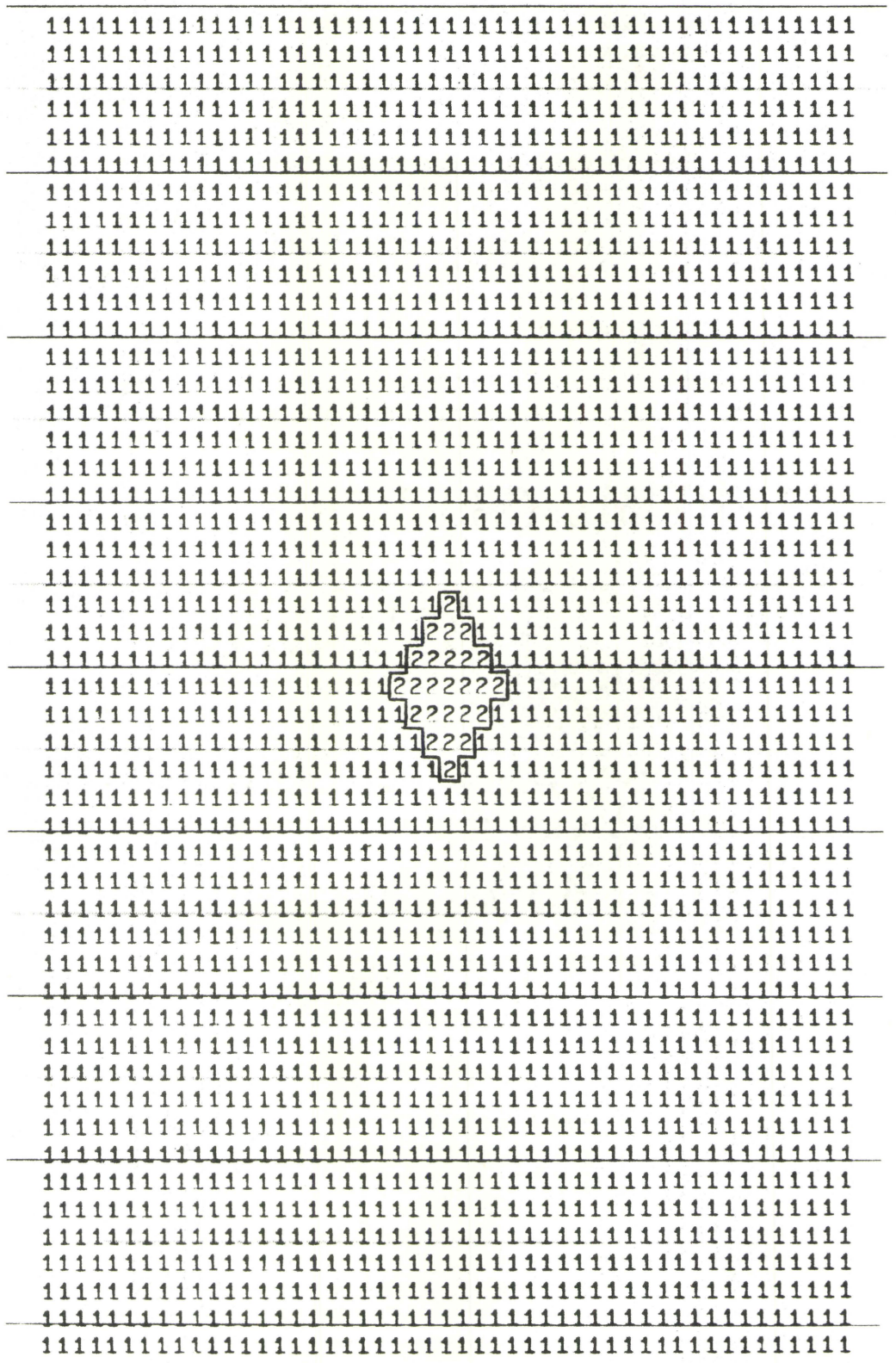


Figure 23(a) - Initial distribution of sites on the surface.

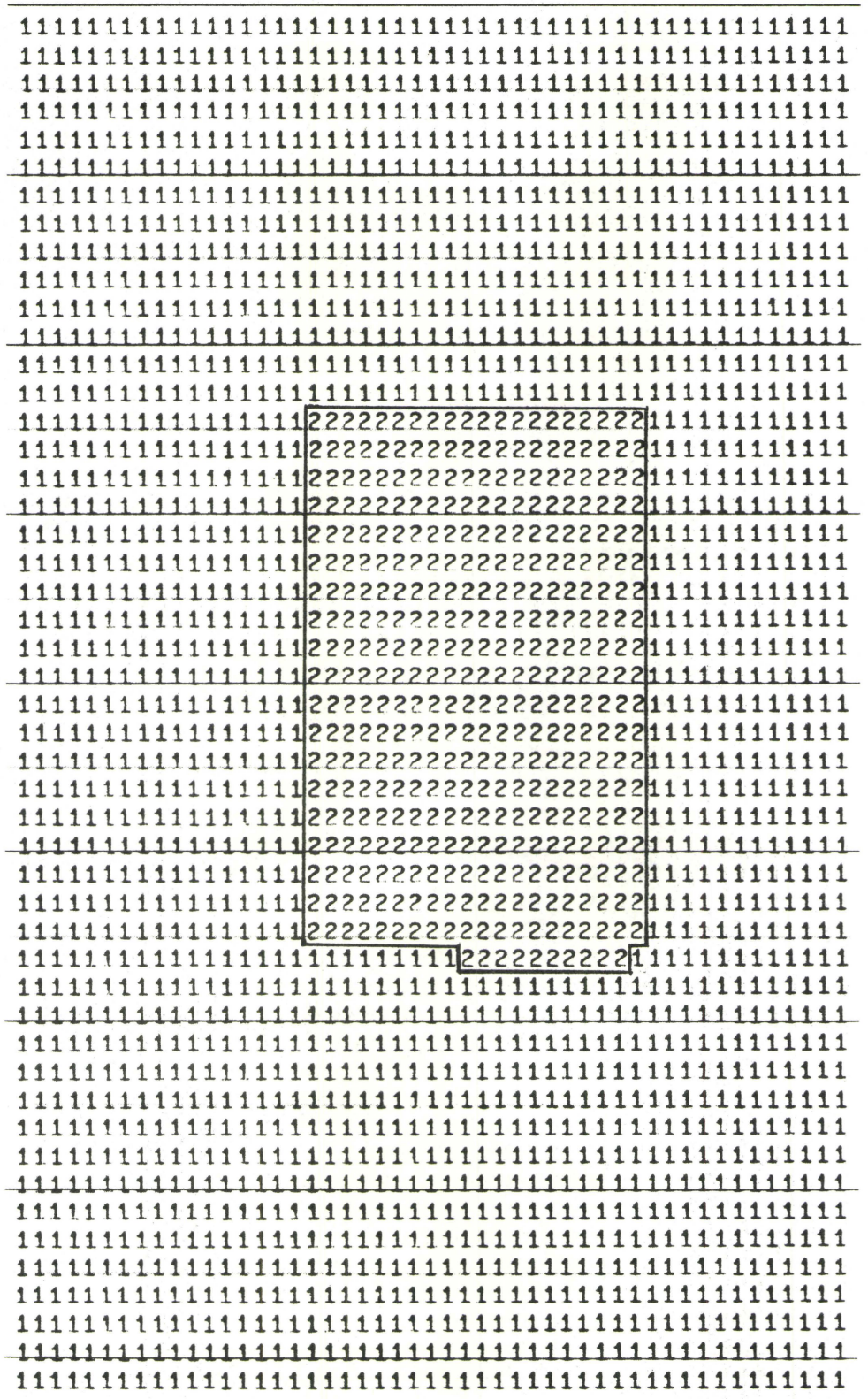


Figure 23(b). Distribution of sites on the surface after 365 removals for the overall probability of kink sites of 0.01.

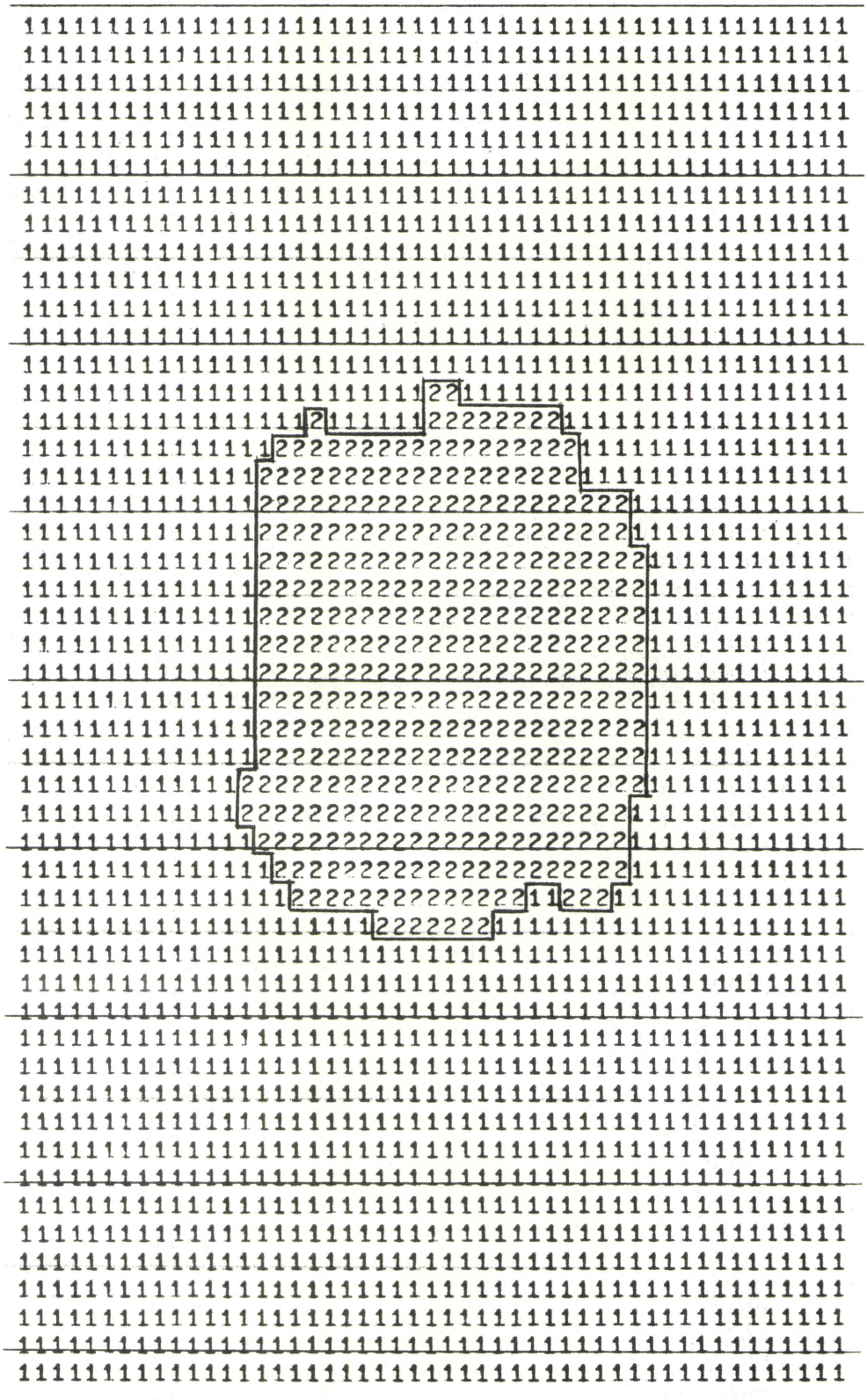


Figure 23(c). Distribution of sites on the surface after 365 removals for the overall probability of kink sites of 1×10^{-4}.