

## A Three-Dimensional Model of Crystal-Growth Disorder

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### Abstract

The relationship between nearest-neighbour growth-disorder models and Ising models is described in detail. The growth model with only two-body interactions is shown to be equivalent, in section perpendicular to the growth direction, to a simple Ising model. Two approximate solutions for the growth model are compared with exact solutions of equivalent Ising models, where possible, and also with computer realizations; the behaviour of these approximate solutions is discussed.

### 1. Introduction

Recent papers (Welberry & Galbraith, 1973, 1975; Welberry, 1977*a,b*) have described two-dimensional models of the introduction of substitutional disorder into crystals during growth. These models have enabled distributions of binary (0,1) variables to be produced from somewhat arbitrary 'growth probabilities'. Our current aim is to extend this work to more realistic three-dimensional models in which the growth probabilities are related specifically to the atomic or molecular interactions in the crystal.

The growth model we consider here is the simplest 3D case, in which the probability that the (0,1) variable  $x_{i,j,k}$  associated with the point  $(i,j,k)$  of a simple cubic lattice depends only on the values of  $x_{i-1,j,k}$ ,  $x_{i,j-1,k}$  and  $x_{i,j,k-1}$ . This is the simplest type of stepwise growth, in which only the three nearest neighbours interact with the growth point; it may also be regarded as a superposition of triangular layers, each point in a new layer depending on three points in a triangle in the previous layer.

The relationship between growth models and general Ising models has already been established (Enting, 1977*a,b,c*; Welberry, 1977*a,b*; Enting & Welberry, 1978); while growth-disorder models are in general special cases of more general Ising models, they themselves may have as special cases Ising models of lower dimensionality. In particular, Welberry & Miller (1978) reported that, in certain 3D nearest-neighbour growth models, individual layers normal to the growth direc-

tion were equivalent to the simple nearest-neighbour Ising model on a triangular lattice, and pairs of successive such (111) layers were similarly equivalent to those on a honeycomb lattice. That paper was primarily concerned with the occurrence of phase transitions in the growth models.

In this paper we derive and expand on the results given in Welberry & Miller (1978), to illustrate the relationship between growth probabilities and interaction energies. We also describe some approximate methods for obtaining correlations and concentrations of the growth models and, where possible, compare the results of these methods with exact solutions of equivalent Ising models.

### 2. Probabilities and energies

The growth model discussed here is the most general case described by the equation

$$\begin{aligned}
 P(x_{i,j,k} = 1 | x_{i-1,j,k}, x_{i,j-1,k}, x_{i,j,k-1}) \\
 = \alpha + \beta x_{i-1,j,k} + \gamma x_{i,j-1,k} + \delta x_{i,j,k-1} \\
 + \epsilon x_{i-1,j,k} x_{i,j-1,k} \\
 + \zeta x_{i,j-1,k} x_{i,j,k-1} + \eta x_{i,j,k-1} x_{i-1,j,k} \\
 + \lambda x_{i-1,j,k} x_{i,j-1,k} x_{i,j,k-1}, \quad (1)
 \end{aligned}$$

where  $x_{i,j,k}$  may take values 0,1. There are thus eight distinct probabilities which we denote  $a, b, \dots, h$ ; this notation is shown in detail in Table 1.

Although equation (1) describes the model, it does not help to relate the probabilities to physical interactions. Instead we shall consider the growth process

Table 1. Probability notation for the growth model

$x_{i-1,j,k}$	$x_{i,j-1,k}$	$x_{i,j,k-1}$	$P(x_{i,j,k} = 1)$
1	1	1	$a$
0	1	1	$b$
1	0	1	$c$
0	0	1	$d$
1	1	0	$e$
0	1	0	$f$
1	0	0	$g$
0	0	0	$h$

itself and apply Boltzmann statistics. The energy involved in adding point  $(i,j,k)$  to the crystal may be denoted  $E_{1;i,j,k}$  or  $E_{0;i,j,k}$  as  $x_{i,j,k}$  is respectively 1 or 0, and the probability that  $x_{i,j,k} = 1$  may thus be written

$$P(x_{i,j,k} = 1 | x_{i-1,j,k}, x_{i,j-1,k}, x_{i,j,k-1}) = \frac{\exp(-E_{1;i,j,k})}{\exp(-E_{0;i,j,k}) + \exp(-E_{1;i,j,k})}. \quad (2)$$

Equations of this type may be written for all values of  $x_{i-1,j,k}$ ,  $x_{i,j-1,k}$  and  $x_{i,j,k-1}$ .

It is convenient to transform here to  $(-1,1)$  variables  $\sigma_{i,j,k}$  defined by  $\sigma_{i,j,k} = 2x_{i,j,k} - 1$ . The energy of the growth point may then be written as

$$E_{x_{i,j,k}} = -\sigma_{i,j,k}(Q + R_1\sigma_{i-1,j,k} + R_2\sigma_{i,j-1,k} + R_3\sigma_{i,j,k-1} + S_1\sigma_{i-1,j,k}\sigma_{i,j-1,k} + S_2\sigma_{i,j-1,k}\sigma_{i,j,k-1} + S_3\sigma_{i,j,k-1}\sigma_{i-1,j,k} + T\sigma_{i-1,j,k}\sigma_{i,j-1,k}\sigma_{i,j,k-1}). \quad (3)$$

For simplicity we assume that the three axes of the model are equivalent, so that  $R_1, R_2, R_3 = R$  and  $S_1, S_2, S_3 = S$  and use the Ising-model convention that positive  $R$  corresponds to a ferromagnetic interaction leading to aggregation of like atoms. The probability of a 1 after three zeros may then be written

$$h = \frac{\exp(+Q - 3R + 3S - T)}{\exp(Q - 3R + 3S - T) + \exp(-Q + 3R - 3S + T)} = \frac{1}{1 + \exp(-2Q + 6R - 6S + 2T)} \quad (4)$$

and the other growth probabilities may similarly be written

$$g, f, d = \frac{1}{1 + \exp(-2Q + 2R + 2S - 2T)}, \quad (5)$$

$$e, c, b = \frac{1}{1 + \exp(-2Q - 2R + 2S + 2T)}, \quad (6)$$

$$a = \frac{1}{1 + \exp(-2Q - 6R - 6S - 2T)}. \quad (7)$$

If we now consider only two-body interactions, and set  $Q, S, T = 0$ , then equations (4)–(7) may simply be written as

$$1 - h = a, \quad (8)$$

$$1 - g = 1 - f = 1 - d = e = c = b, \quad (9)$$

where  $a$  and  $b$  are related by

$$a/(1 - a) = [b/(1 - b)]^3. \quad (10)$$

In two dimensions a similar treatment based on two-body nearest-neighbour interactions gives rise to a linear growth model, in which the growth probabilities

may be expressed as linear functions of  $x_{i-1,j}$  and  $x_{i,j-1}$ ; considering equation (1), this would involve setting  $\delta, \epsilon, \zeta, \eta$  and  $\lambda$  equal to zero. An exact solution of this model, in which the concentration and all correlation coefficients are expressed as functions of  $\alpha, \beta$  and  $\gamma$ , was obtained by Welberry & Galbraith (1973), following work by Whittle (1954) and Bartlett (1967, 1968). The growth model generated by equations (8)–(10) is, however, not linear, and no exact general solution exists; in the next section we show that by relating the growth model to a soluble Ising model the concentration and some of the correlations may be determined.

### 3. Ising formulation

The method described here is an extension of that developed by Welberry (1977a) and Enting (1977b) in the study of some symmetry-dependent solutions of two-dimensional growth models. The argument will be followed at a very general level to relate the Ising-model parameters to the coefficients of equation (3) before discussion of some simpler special cases.

Consider an infinite three-dimensional array and associate with each point a variable  $\sigma_{i,j,k}$  which initially has value  $-1$  at all points. Now select four adjacent points  $A, B, C, X$  as illustrated in Fig. 1 and let the  $\sigma_{i,j,k}$  of these points take values  $-1$  or  $1$ . Including only interactions within tetrahedra such as  $ABCX$  then the total interaction energy of this infinite array may be written as

$$E = -\sum_i \sum_j \sum_k \{ H\sigma_{i,j,k} + J_1\sigma_{i,j,k}\sigma_{i-1,j,k} + J_2\sigma_{i,j,k}\sigma_{i,j-1,k} + J_3\sigma_{i,j,k}\sigma_{i,j,k-1} + J_4\sigma_{i-1,j,k}\sigma_{i,j-1,k} + J_5\sigma_{i,j-1,k}\sigma_{i,j,k-1} + J_6\sigma_{i,j,k-1}\sigma_{i-1,j,k} + L_1\sigma_{i,j,k}\sigma_{i-1,j,k}\sigma_{i,j-1,k} + L_2\sigma_{i,j,k}\sigma_{i,j-1,k}\sigma_{i,j,k-1} + L_3\sigma_{i,j,k}\sigma_{i,j,k-1}\sigma_{i-1,j,k} + L_4\sigma_{i-1,j,k}\sigma_{i,j-1,k}\sigma_{i,j,k-1} + K\sigma_{i,j,k}\sigma_{i-1,j,k}\sigma_{i,j-1,k}\sigma_{i,j,k-1} \}. \quad (11)$$

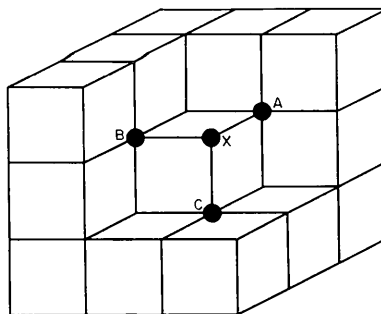


Fig. 1. Notation for the simple nearest-neighbour growth model, in which  $X$  depends only on  $A, B, C$ .

The relationship between the coefficients  $H, J_1$ , etc. and interactions within tetrahedra such as  $ABCX$  is summarized in Table 2.

The energy is related to the growth probabilities using the equation

$$\prod_i \prod_j \prod_k P(x_{i,j,k} = 1 | x_{i-1,j,k}, x_{i,j-1,k}, x_{i,j,k-1}) = \frac{\exp(-E)}{Z}, \quad (12)$$

where  $Z$  is a constant (the partition function) for given  $H, J_1$ , etc. and  $\sigma_{i,j,k} = 2x_{i,j,k} - 1$ . Taking logarithms of both sides, equation (12) becomes

$$\sum_i \sum_j \sum_k \ln[P(x_{i,j,k} = 1 | x_{i-1,j,k}, x_{i,j-1,k}, x_{i,j,k-1})] = -\ln(Z) - E. \quad (13)$$

For practical purposes the infinite three-dimensional array is represented by a  $4 \times 4 \times 4$  array, with summations of  $i, j, k$  over the range 2 to 4; this covers all the interactions involving the points of one tetrahedron.

There are in all sixteen equations of the form of (13), and the coefficients of these were determined using a computer program. The first equation, when all  $\sigma_{i,j,k} = -1$ , is simply

$$27 \ln(1-h) = -27(-H + J_1 + J_2 + J_3 + J_4 + J_5 + J_6 - L_1 - L_2 - L_3 - L_4 + K) - \ln(Z), \quad (14)$$

and this is subtracted from all the others to eliminate the constant term. The four equations for the cases where only one of the  $\sigma_{i,j,k}$  equals 1 are identical, leaving twelve distinct equations relating the growth probabilities to the Ising-model energy terms. After some rearrangement these equations may be written in matrix form as

$$\begin{bmatrix} H \\ J_1 \\ J_2 \\ J_3 \\ J_4 \\ J_5 \\ J_6 \\ L_1 \\ L_2 \\ L_3 \\ L_4 \\ K \end{bmatrix} = \frac{1}{16} \begin{bmatrix} -4 & -2 & -2 & -2 & 0 & 0 & 0 & 2 & -2 & 0 & 0 & 0 & 2 & 2 & 2 & 4 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 & -1 & 1 & -1 & 1 & 1 & -1 & 1 \\ 1 & 1 & 1 & -1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & -1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 & -1 & 1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & -1 & 1 \\ 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 \\ -1 & 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & 1 & -1 & 1 \\ -1 & -1 & 1 & 1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 & -1 & -1 & 1 & -1 & 1 \\ -1 & 1 & -1 & 1 & 1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 \\ -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 \\ 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 \end{bmatrix} \begin{bmatrix} \ln(1-h) \\ \ln(1-g) \\ \ln(1-f) \\ \ln(1-d) \\ \ln(1-e) \\ \ln(1-b) \\ \ln(1-c) \\ \ln(1-a) \\ \ln(h) \\ \ln(g) \\ \ln(f) \\ \ln(d) \\ \ln(e) \\ \ln(b) \\ \ln(c) \\ \ln(a) \end{bmatrix} \quad (15)$$

This equation covers the most general case; we shall now consider the effect of some conditions on it.

We first impose the condition that the model must be invariant to the interchange of  $\sigma = 1$  and  $\sigma = -1$ . This gives the following relations between the growth probabilities:

$$\begin{aligned} 1-h &= a; & 1-g &= b \\ 1-f &= c; & 1-d &= e, \end{aligned} \quad (16)$$

and for this case equation (15) becomes

$$\begin{bmatrix} H \\ J_1 \\ J_2 \\ J_3 \\ J_4 \\ J_5 \\ J_6 \\ L_1 \\ L_2 \\ L_3 \\ L_4 \\ K \end{bmatrix} = \frac{1}{8} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 \\ 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\ 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \ln(a) \\ \ln(b) \\ \ln(c) \\ \ln(e) \\ \ln(1-a) \\ \ln(1-b) \\ \ln(1-c) \\ \ln(1-e) \end{bmatrix} \quad (17)$$

The reversibility condition thus has the effect of setting equal to zero the interactions  $H, L_1, L_2, L_3, L_4$  which involve an odd number of points. The remaining interactions are  $J_1, J_2, J_3$  which are two-body interactions

Table 2. Interactions between points of tetrahedra such as  $ABCX$  of Fig. 1 represented by coefficients of equations (3) and (11)

Interaction between points	Coefficient equation (3)	Coefficient equation (11)
$X$	$Q$	$H$
$XA$	$R_1$	$J_1$
$XB$	$R_2$	$J_2$
$XC$	$R_3$	$J_3$
$AB$	—	$J_4$
$BC$	—	$J_5$
$CA$	—	$J_6$
$XAB$	$S_1$	$L_1$
$XBC$	$S_2$	$L_2$
$XCA$	$S_3$	$L_3$
$ABC$	—	$L_4$
$XABC$	$T$	$K$

between points in adjacent (111) layers;  $J_4, J_5, J_6$ , two-body interactions between nearest-neighbours within a (111) layer; and the four-body interaction  $K$  between three points in a (111) layer and one point in the subsequent layer.

For this model we may also make a comparison between the coefficients of the Ising-model equation (11) and the coefficients of equation (3), describing the energy of the growth model. From this we find that

$$\begin{aligned} Q = H = 0; \quad R_1 = J_1 \\ R_2 = J_2; \quad R_3 = J_3 \\ T = K; \quad S_1, S_2, S_3 = L_1, L_2, L_3 = 0. \end{aligned} \quad (18)$$

If we now include the equivalence of the three axes as a further condition, so that  $b = c = e$ , then the non-zero parts of (17) become

$$J_1, J_2, J_3 = \frac{1}{8} \ln \left[ \frac{a}{1-a} \frac{b}{1-b} \right], \quad (19)$$

$$J_4, J_5, J_6 = \frac{1}{8} \ln \left[ \frac{a(1-a)}{b(1-b)} \right], \quad (20)$$

$$K = \frac{1}{8} \ln \left[ \frac{a}{1-a} \left( \frac{1-b}{b} \right)^3 \right]. \quad (21)$$

For the growth model based on two-body interactions, for which equation (10) is valid, then  $K = 0$ ; we may also note that this model is invariant to reflection in the (111) plane. If we isolate a pair of successive (111) layers forming a puckered two-dimensional honeycomb lattice the two sets of  $J_4, J_5, J_6$  interactions within this double layer can be considered as cancelling the two sets of  $J_1, J_2, J_3$  interactions linking the selected double layer to the rest of the lattice. This result is obtained from the star-triangle transformation (Syozzi, 1972) which may be used to show that  $J_1, J_2, J_3$  on the honeycomb lattice are equivalent to  $-J_4, -J_5, -J_6$  on a triangular lattice. Any double (111) layer may thus be 'decoupled' from the remainder of the three-dimensional lattice, and by a

similar argument an individual (111) layer may be regarded as a two-dimensional triangular lattice decoupled from the rest of the three-dimensional model.

The three-dimensional growth-disorder model may thus be regarded as a stack of decoupled two-dimensional nearest-neighbour Ising models on either the triangular or honeycomb lattices, provided that the growth model is based only on two-body interactions. These Ising models have been solved (Houtappel, 1950; Potts, 1952), and these solutions may be used to obtain the concentration and [100] and [110] correlations of the growth model. In addition, and most importantly, the critical point may be determined.

We shall now briefly consider the application of (17) to some cases for which the interactions  $J_1, J_2, J_3$  are not all equal. For example, suppose one of the [110] interactions is constrained to be zero. If  $J_4 = 0$  and  $J_5 = J_6$ , then from (17) we may write

$$J_4 = \frac{1}{8} \ln \left[ \frac{bc(1-b)(1-c)}{ae(1-a)(1-e)} \right] = \ln(1), \quad (22)$$

and since the equality of  $J_5$  and  $J_6$  implies  $b = c$  this equation may be simplified to

$$b^2(1-b)^2 = ae(1-a)(1-e), \quad (23)$$

which may only be satisfied by setting  $b = a, e = 1 - a$ . Equation (1) thus reduces to a two-dimensional growth model, while the only non-zero interaction of (17) is

$$J_3 = \frac{1}{8} \ln \left[ \frac{e(1-a)(1-b)(1-c)}{abc(1-e)} \right] = \frac{1}{2} \ln \left[ \frac{a}{1-a} \right], \quad (24)$$

all the other terms reducing to zero. This growth model is thus equivalent in (11) section to a one-dimensional Ising model.

We shall now consider the location of the critical points in some more general cases, and we start by introducing the notation

$$S_u = \sinh(2J_u); \quad C_u = \cosh(2J_u), \quad (25)$$

for  $u = 1, 2, \dots, 6$ . From Syozzi (1972) the equations for the star-triangle transformation are

$$\begin{aligned} S_4^2 &= 4(S_1 S_2)^2 / A^4, \\ S_5^2 &= 4(S_2 S_3)^2 / A^4, \\ S_6^2 &= 4(S_3 S_1)^2 / A^4, \end{aligned} \quad (26)$$

where  $A^4 = 4(S_1^2 + S_2^2 + S_3^2 + 2C_1 C_2 C_3 + 2)$ . From the same source, the equations which must be satisfied at the critical point are

$$\begin{aligned} C_1 &= -C_2 C_3 + S_2 S_3 C_1, \\ C_2 &= -C_3 C_1 + S_3 S_1 C_2, \\ C_3 &= -C_1 C_2 + S_1 S_2 C_3. \end{aligned} \quad (27)$$

One obvious simple case to investigate is when  $S_1 = S_2 = S_3/q$ . Then  $C_1 = C_2$  and equations (27) reduce to

$$\begin{aligned} C_1 &= -C_1C_3 + qS_1^2C_1, \\ C_3 &= -C_1^2 + S_1^2c_3, \end{aligned} \tag{28}$$

from which the critical point is defined by

$$S_1(\text{critical}) = \left( \frac{2+q}{q} \right)^{1/2}. \tag{29}$$

The results for several values of  $q$  are summarized in Table 3.

Imposing a relationship between hyperbolic functions of the interaction parameters is convenient but hardly realistic. However, if we consider series of the form  $J_1 = J_2 = J_3/q$  we may obtain the growth probabilities using equations such as (4)–(7), and then use an iterative method to solve equations (27) and locate the critical point. The critical values for  $J_1, J_3$  and corresponding growth probabilities were determined for several values of  $q$ , and these results are summarized in Table 4.

The equivalence between 3D nearest-neighbour growth models based on two-body interactions and some simple 2D nearest-neighbour Ising models has enabled us to calculate exact values for many of the parameters of these growth models. However, for more complicated growth-disorder models we must use approximate methods such as those described in the next section.

Table 3. *Critical points for series of the form  $\sinh(2J_1) = \sinh(2J_2) = \sinh(2J_3)/q$*

$q$	Growth probabilities at the critical point		
	$a$	$b, c$	$d$
3	0.9854	0.8873	0.5206
2	0.9830	0.8536	0.6294
1	0.9811	0.7887	0.7887
$\frac{1}{2}$	0.9829	0.7236	0.8935
$\frac{1}{3}$	0.9852	0.6890	0.9312
$-\frac{1}{3}$		no critical point	
$-\frac{1}{2}$		no critical point	
-1		no critical point	
-2		no critical point	
-3	0.4456	0.2113	0.9180

Table 4. *Critical points of series  $Q_1 = Q_2 = Q_3/r$  ( $Q_1 > 0$ )*

$r$	$Q_1$	$Q_3$
3	0.4812	1.4436
2	0.5306	1.0613
1	0.6585	0.6585
$\frac{1}{2}$	0.8314	0.4157
$\frac{1}{3}$	0.9495	0.3165
$-\frac{1}{3}$	0.9495	-0.3165
$-\frac{1}{2}$	0.8314	-0.4157
-1	0.6585	-0.6585
-2	0.5306	-1.0613
-3	0.4812	-1.4436

#### 4. Approximate methods

The two methods described in this section both depend on triangular groups of points in the (111) layers, first of three points and then of six. The basic method is similar to the ‘matched boundary’ technique of Welberry & Miller (1977) for the solution of some two-dimensional growth-disorder models. Only the three-point method will be described in detail, since the same principles are common to both methods.

We consider three adjacent points  $A, B, C$  in a (111) plane of the lattice and investigate the transition to three points  $A', B', C'$  in the subsequent layer; this notation is illustrated in Fig. 2. To estimate the probabilities of various  $A', B', C'$  we also need to know the conditional distribution of points  $D, E, F$  given  $A, B, C$ , and this is where we require a satisfactory approximation.

The frequency of occurrence of various triplets  $A, B, C$  may be denoted by  $f_1, f_2, \dots, f_8$  as illustrated in Fig. 3. For the general three-dimensional growth model we have the equations

$$\begin{aligned} \theta &= f_2 + f_4 + f_6 + f_8 \\ &= f_3 + f_4 + f_7 + f_8 \\ &= f_5 + f_6 + f_7 + f_8, \end{aligned} \tag{30}$$

where  $\theta$  is the concentration of ones. The nearest-neighbour and next-nearest-neighbour probabilities may be written as

$$P_{100} = gf_2 + ef_4 + cf_6 + af_8, \tag{31}$$

$$P_{010} = ff_3 + ef_4 + bf_7 + af_8, \tag{32}$$

$$P_{001} = df_5 + cf_6 + bf_7 + af_8, \tag{33}$$

$$P_{1\bar{1}0} = f_4 + f_8, \tag{34}$$

$$P_{\bar{1}01} = f_6 + f_8, \tag{35}$$

$$P_{01\bar{1}} = f_7 + f_8, \tag{36}$$

where, for example,  $P_{001}$  is the probability that both  $x_{i,j,k}$  and  $x_{i,j,k-1} = 1$  and  $P_{1\bar{1}0}$  is the probability that both  $x_{i,j,k}$  and  $x_{i-1,j+1,k} = 1$ . We also have the equation

$$\sum_{q=1}^8 f_q = 1. \tag{37}$$

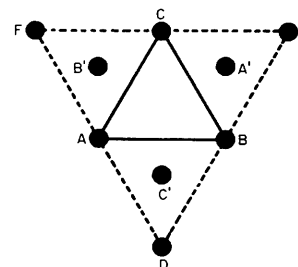


Fig. 2. Notation for the three-point approximate method.

For the triangular-lattice simple Ising model, the frequencies of triangles  $ABC$  also apply to triangles  $A'B'C'$  as illustrated in Fig. 3, and hence these frequencies may be used to obtain the required distributions of  $D, E, F$ . As an example, the probability that  $C' = 1$  is given by

$$P(C' = 1|A, B) = [P(C' = 1|D = 1, A, B)f_r + P(C' = 1|D = 0, A, B)f_s]/(f_r + f_s), \quad (38)$$

where  $r$  and  $s$  take appropriate values; if  $A = 1$  and  $B = 0$ , for instance, then  $r = 7$  and  $s = 3$ .

The probability of each possible triplet  $A'B'C'$  for given  $A, B, C$  is thus the product of three equations of the same form as (38). We may then write in matrix form the probability of each  $A'B'C'$  given each  $ABC$ —this matrix will be denoted by  $Z$  with elements  $z_{rs}$ . If the matrix of frequencies is denoted by  $F$ , with elements  $f_r$ , then

$$F = Z \times F. \quad (39)$$

This suggests the possibility of determining the  $f_r$  by an iterative process.

Since the calculation of  $Z$  itself involves  $F$ , two levels of iteration are necessary. Assuming the initial values of the  $f_r$  to be given, values of the  $z_{rs}$  are calculated and the stationary vector ( $F'$ ) of this matrix found, either by iteration or by a powering method. The  $f_r'$  values are then used to calculate a new transition matrix  $Z'$  and the stationary vector of this is found. The process continues until a completely stationary solution is reached, and the concentration and correlations are then calculated using equations (30)–(36).

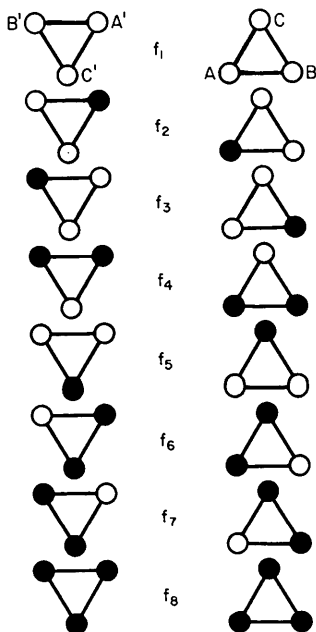


Fig. 3. Triangular frequency notation for three-point approximate method.

In the six-point method we consider the transition from points  $A, B, C, D, E, F$  to points  $A', B', C', D', E', F'$  in the subsequent layer; this notation is illustrated in Fig. 4. For this method we assume that the frequencies of occurrence of the various sextets are the same as those of their inverted images, just as for the three-point method. The equations corresponding to (38) then involve eight terms on the r.h.s. instead of two. The next possibility after the six-point method is one involving ten points, illustrated in Fig. 5, but the computer space and time required for this would be very large and we have not investigated it. The figure used for the six-point method is the same as the outer figure, including dashed lines, for the three-point method (see Figs. 2 and 4). There is a similar relationship between the figures for the six-point and suggested ten-point methods (Figs. 4 and 5) and this may be extended to larger numbers of points, if required.

Enting (1977*d*) has pointed out that the three-point method described here is equivalent to the application to the triangular Ising model of the Kikuchi approximation described by Hijmans & De Boer (1955). In this method the energy of the system is considered to be

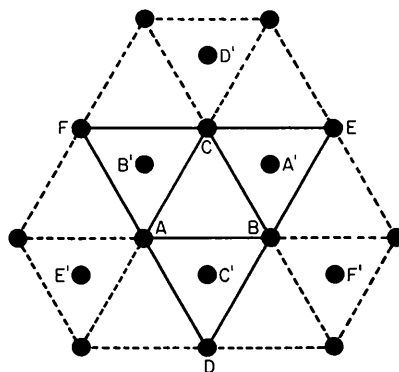


Fig. 4. Notation for the six-point approximate method.

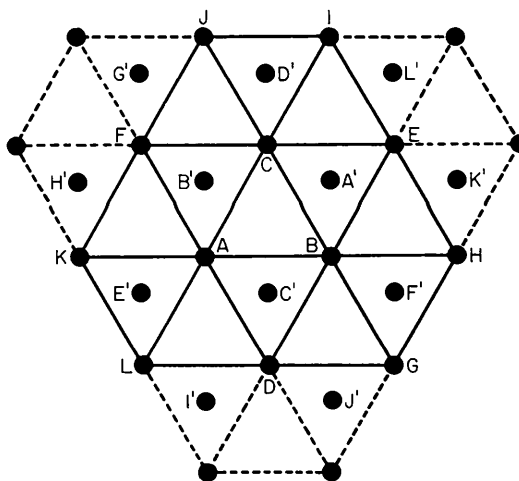


Fig. 5. Possible ten-point approximate method.

a linear combination of the energies of  $m$ -figure assemblies, corresponding to the basic figure and a series of smaller subfigures. Each  $m$ -figure assembly consists of  $N$  independent figures of type  $m$ , distributed over their configurations as figures of the same type are distributed within the lattice.

Hijmans & De Boer (1955) considered in detail the application of this method to the triangular-lattice simple Ising model, and showed that using a rhombus of four points as the basic figure gave exactly the same results as using a triangle of three points. The results they obtained are exactly equivalent to the method described here, in which the distribution of triangles such as  $ABD$  of Fig. 3 is calculated from the distribution of triangles such as  $ABC$ .

In the next section we shall consider the application of our approximate methods to models for which exact Ising solutions are available, but we may note here that our three-point method predicts exactly the same critical point as does the Kikuchi method based on either the triangle or the rhombus. Our six-point method could probably also be related to a Kikuchi approximation, but we have not investigated this.

### 5. Comparison of approximate methods and Ising solutions

We consider here the application of the three-point and six-point iterative methods to growth models defined by equations (8)–(10), for which exact values of the concentration and some correlation coefficients may be obtained from Ising-model solutions (Houtappel, 1950; Potts, 1952).

The concentration  $\theta$  of the growth model is related to the magnetization  $m$  of the Ising model by  $m = 2\theta - 1$ . For the correlation coefficients we may note that, for the growth model, they are defined by

$$r_{u,v} = (P_{u,v} - \theta^2)/(\theta - \theta^2), \quad (40)$$

where  $P_{u,v}$  is the probability that both  $x_u$  and  $x_v$  equal 1. For the (0,1) variables of the growth model this probability is equal to  $E(x_u x_v)$ , the expectation value of their product. Transforming to the (-1,1) variables of the Ising model, we find (Bartlett, 1976)

$$r_{u,v} = [E(\sigma_u \sigma_v) - m^2]/(1 - m^2), \quad (41)$$

so that when  $m = 0$  the coefficient of correlation between two points is equal to the expectation value of the product of their spin variables. Below the critical point this equality does not hold, the correlation coefficient decreasing while  $E(\sigma_u \sigma_v)$  increases. The models considered here have the three axes equivalent, so we may write

$$r_1 = r_{100}, r_{010}, r_{001}, \quad (42)$$

$$r_2 = r_{1\bar{1}0}, r_{0\bar{1}\bar{1}}, r_{\bar{1}0\bar{1}}, \quad (43)$$

and the corresponding expectation values of products of spins as  $r'_1, r'_2$ .

The computer programs used to obtain the results presented here follow the description given in § 4. For the three-point method this is adequate, but for the six-point one it produced some complications. For instance, the model with  $b = 0.875$  failed to converge (the convergence condition was that the change in all  $f_i$  be less than 0.000001) and became cyclic, probably because of round-off errors, and the models with  $b = 0.775$  and 0.95 converged very slowly, in the former case because it is very close to the critical point given by this method. However, by modifying the iteration process slightly, the speed of convergence may be greatly increased. The initial frequency distribution used here corresponded to a model with zero correlation and a concentration of 0.75 ( $a, b, \dots, h = 0.75$ ); the results obtained with an initial distribution corresponding to a random model with  $\theta = 0.5$  will be discussed later.

The results obtained using the two methods are illustrated in Figs. 6 and 7, which also show the exact values obtained from the Ising solutions. Fig. 6 shows some of the concentration values in the region of the critical point, and it is apparent that the iterative methods provide a good approximation to the actual behaviour of the Ising and growth models. Fig. 7 illustrates the behaviour of the nearest-neighbour correlation coefficient  $r_1$  – the results for  $r_2$  are qualitatively similar and are not shown here.

The critical point of the Ising model marks the point at which, with decreasing temperature, the structure of the model becomes determined by long-range interactions instead of short-range ones, and at the critical point the correlation length is infinite. The critical point given by methods involving only a few points may thus

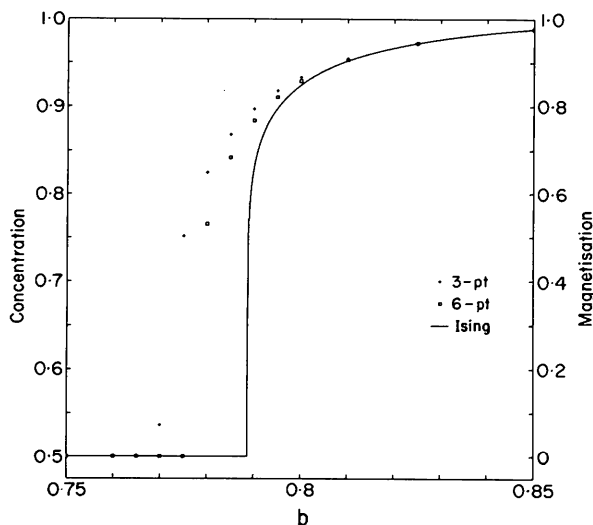


Fig. 6. Concentration and magnetization vs  $b$  for Ising series – exact solution and approximate methods.

be regarded as the point where the correlation length exceeds the dimension of the model. Approximate solutions involving only a few points will obviously not be very accurate in the neighbourhood of the critical point, but it is necessary to strike a balance between accuracy and the availability of computing resources.

The results described above were obtained using an initial concentration of 0.5 and zero correlations ( $a, b, \dots, h = 0.5$ ) the iterative methods may converge to an unstable solution below the critical point. Above the critical temperature there is one stationary value, the minimum at  $\theta = 0.5$ . Below the critical temperature there are the two minima corresponding to the ordered solutions, but there is a third stationary value at  $\theta = 0.5$  which must also represent a valid, though unstable, solution of the model. The results obtained using these unstable solutions correspond in magnitude to those obtained when the iterative methods are applied to 'antiferromagnetic' growth models, for which  $\theta$  is always 0.5.

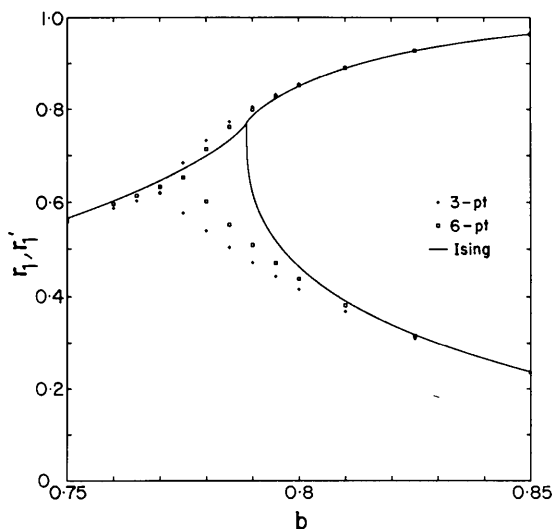


Fig. 7. Nearest-neighbour correlation and spin-product expectation for Ising series – exact solution and approximate methods.

## 6. Approximate solutions of non-Ising models

By non-Ising models we refer to those growth models for which there is no simple, or more importantly no soluble, equivalent Ising model. A convenient way of generating such models is to consider the ones generated by equations (8) and (9) without the restriction of (10), so that  $a$  and  $b$  may independently range from 0 to 1. This, as we have seen, is equivalent to setting  $Q, S_1, S_2, S_3$  equal to zero in equation (3), with non-zero two-point and four-point interactions.

Instead of (10) we now have the equation

$$a/(1-a) = [b/(1-b)]^3/q, \quad (44)$$

which gives a series of curves including the Ising series ( $q = 1$ ). It would undoubtedly be more realistic to impose conditions on the energy terms, such as  $T = R/q$ , but equation (44) gives series which are convenient for investigating the behaviour of the approximate methods over the range of  $a$  and  $b$ . We have so far considered only the location of the critical points of these series, comparing the approximate methods with computer realizations. However, Welberry & Miller (1978) showed that this is not sensitive to the exact location of the critical point since convergence to a stationary state becomes very slow in its neighbourhood. The results of these comparisons are summarized in Table 5.

The estimated accuracy of the critical points determined from the computer realizations is presented in Table 5 as an estimated standard deviation or 67% confidence limit. For the  $b = 1$  series this determination is very imprecise, but for the others it seems possible to locate the critical points to an accuracy of about  $\pm 0.01$  in the probabilities, and to this degree of accuracy the results obtained from the six-point method agree quite well with the realizations. For the three-point method, however, the agreement becomes poor for large values of  $q$ , and for the  $b = 1$  ( $q = \infty$ ) series the critical value of  $a$  obtained by this method is too small by about 0.1.

Table 5. Critical points determined by various methods

$$\frac{a}{1-a} = \left( \frac{b}{1-b} \right)^3 / q$$

$q$	Three-point	Six-point	Realization
$\infty$ ( $b = 1$ )	$0.730 < a_{\text{crit}} < 0.735$	$0.830 < a_{\text{crit}} < 0.840$	$a_{\text{crit}} = 0.83 \pm 0.01$
100	$0.895 < b_{\text{crit}} < 0.8975$	$0.905 < b_{\text{crit}} < 0.910$	$b_{\text{crit}} = 0.910 \pm 0.005$
10	$0.830 < b_{\text{crit}} < 0.835$	$0.840 < b_{\text{crit}} < 0.850$	$b_{\text{crit}} = 0.855 \pm 0.005$
1	$0.765 < b_{\text{crit}} < 0.770$	$0.775 < b_{\text{crit}} < 0.780$	$b_{\text{crit}} = 0.790 \pm 0.005^*$
0.1	$0.705 < b_{\text{crit}} < 0.710$	$0.705 < b_{\text{crit}} < 0.715$	—
0 ( $a = 1$ )	$0.665 < b_{\text{crit}} < 0.670$	$0.665 < b_{\text{crit}} < 0.670$	$b_{\text{crit}} = 2/3^\dagger$

\* The exact critical point is at  $b = 0.7887$  for this series.

† See discussion of this series in text.



The  $a = 1$  ( $q = 0$ ) series is a special case for which it appears that the three-point and six-point methods agree both with each other and with the computer realizations. The partially deterministic nature of this model, with probabilities taking values 0 and 1, gives rise to one particular result which is discussed below.

Consider a cluster of  $N$  ones in a (111) layer surrounded by a sea of zeros and sum the probabilities of having ones in the subsequent layer. Since the probability of a one after three zeros is zero all ones in the new layer must arise from the cluster. We find that for  $b < \frac{2}{3}$  this sum is greater than  $N$  while for  $b > \frac{2}{3}$  it is less. In other words, assuming  $b_{\text{critical}} = \frac{2}{3}$ , above the critical point an isolated cluster will probably grow, while below the critical point it will probably shrink. ('Above' and 'below' refer to temperature – in our case 'below' means towards the totally ordered state, with  $a, b = 1$ , and 'above' means towards a more random model.) No general proof of this result has been obtained but it is true for every example we have tried.

The behaviour of this series may thus be summarized quite simply. For the whole range ( $0 \leq b \leq 1$ ) there are three possible solutions, with concentrations  $0, \frac{1}{2}, 1$ . For  $b < \frac{2}{3}$  the two ordered solutions represent an unstable equilibrium – should the system be put into either of these states it will remain there, but they will not arise through normal operation of the growth process. For  $b > \frac{2}{3}$  the ordered solutions – either all ones or all zeros – represent the stable states of the system, and any computer realization will eventually reach one or other

of them. We may also note that the critical point for this series corresponds to the extreme value of the linear model; there is a similarity here with the two-dimensional linear model, for which the critical point is also at the extreme value.

## 7. Computer realizations

The critical points given in the previous section were determined using computer realizations of 100 layers, each layer consisting of  $250 \times 250$  points with periodic boundary conditions. Fig. 8 shows sections of the 100th layers of some of these realizations. The illustrations are for the critical regions of the  $A = 1$  ( $q = 0$ ) series, the Ising ( $q = 1$ ) series and the  $q = 100$  series. The change in appearance of the sections with increasing  $q$  is noticeable, with the large ordered regions of  $q = 0$  being replaced by scattered individual points or small groups of the minor component for  $q = 100$ . The concentrations and correlations of the illustrated layers are given in Table 6; Figs. 9, 10 and 11 show how the concentration varies with layer number for several examples from each series, and here the difference in behaviour of the  $A = 1$  series is apparent.

Table 6. Numerical parameters for layers illustrated in Fig. 8

$q$	$b$	$\theta$	$r_1$	$r_2$	$f_8$
1	0.77	0.6917	0.6069	0.4232	0.4937
1	0.785	0.8364	0.5694	0.3819	0.6916
1	0.8	0.9180	0.4910	0.2965	0.8234
0	0.65	0.6672	0.6405	0.4669	0.4849
0	0.67	0.8029	0.6844	0.5280	0.6852
0	0.7	0.9062	0.7400	0.6020	0.8525
100	0.905	0.6933	0.4823	0.3001	0.4454
100	0.91	0.8073	0.3866	0.2087	0.5890
100	0.92	0.9037	0.2297	0.0705	0.7520

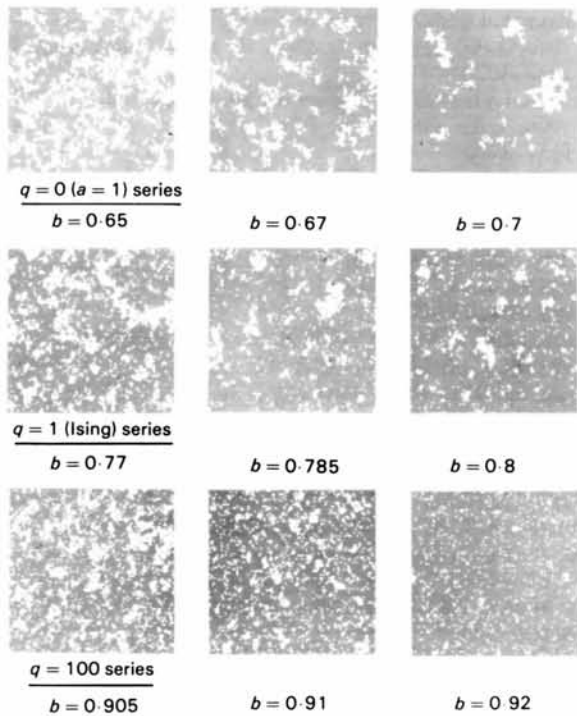


Fig. 8. Sections of the 100th (111) layer for various growth-disorder models.

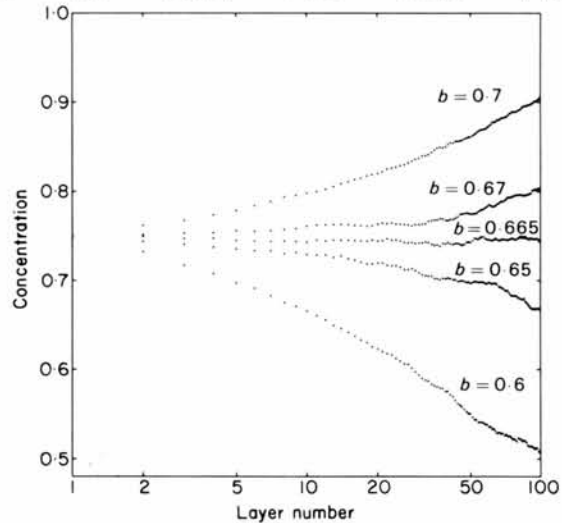


Fig. 9. Concentration vs layer number for various growth models of the  $q = 0$  ( $a = 1$ ) series.

### 8. Discussion

In this paper we have shown how the growth probabilities of our model may be derived from the interaction energies of the growth process, and also how they are related to the parameters of an Ising-model formulation. We have also demonstrated, as reported by Welberry & Miller (1978), that in section perpendicular to the growth direction, the growth model with only two-body nearest-neighbour interactions is equivalent to a simple Ising model, and we have shown that the concentration and some correlations of the growth model may be obtained from exact solutions of an equivalent Ising model.

In the second part of this paper we have described two approximate methods of solving the growth model

to obtain the concentration and some of the correlations, and compared the values obtained by these methods with those obtained from exact solutions of Ising models. We have also considered the application of these approximate methods to more general growth models which include a four-point interaction by using them to determine the critical points of several series. In this case the approximate methods were compared with computer realizations of the growth models.

This comparison shows reasonable agreement between the six-point approximate method and the computer realizations for the whole range studied (see Table 5). For the three-point method, however, the agreement ranges from apparently exact ( $q = 0$ ) to very poor ( $q = \infty$ ). The three-point method operates on the basic building blocks of a triangular lattice and the assumptions required to make it work apparently impose much more severe, and unrealistic, constraints than they do on the six-point method. The apparently exact agreement of both approximate methods with experiment for the  $A = 1$  series is presumably a consequence of the partially deterministic nature of those models.

The authors have benefited from numerous discussions with Dr I. G. Enting.

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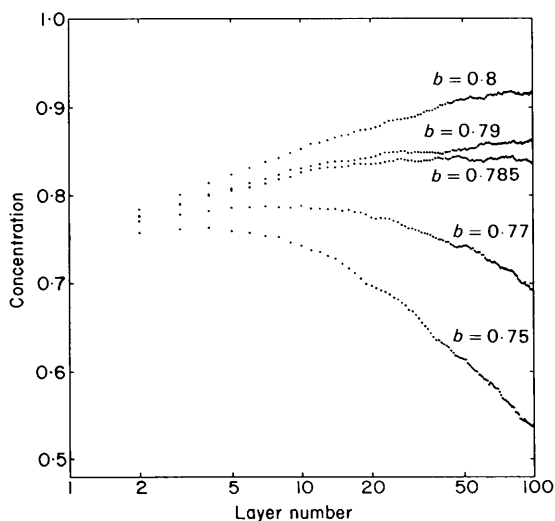


Fig. 10. Concentration vs layer number for various growth models of the  $q = 1$  (Ising) series.

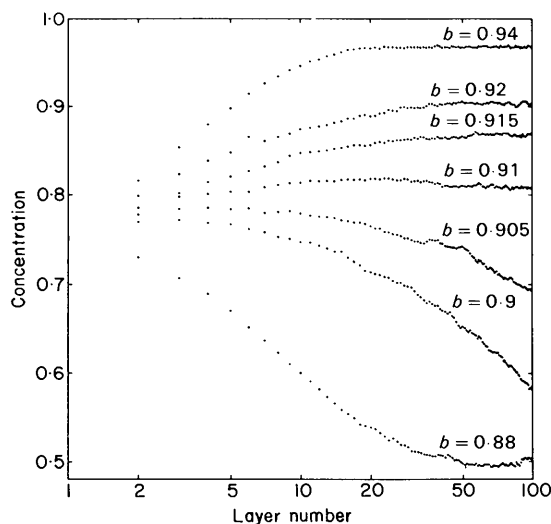


Fig. 11. Concentration vs layer number for various growth models of the  $q = 100$  series.