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Seven Basic Regimes of Steady Crystal Growth in Two Dimensions

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Using a Markov rate-process model, exact expressions are found for the steady growth rate of an edge of a two-dimensional crystal in terms of the number M of particles along the edge, the height difference (or number of permanent steps) K along the edge, the nucleation rate α, and the speed $\alpha + \nu$ of movement of steps. The familiar growth regimes can be identified with asymptotic regimes for the parameters K, $(\nu/\alpha)^{1/2}$, and M. From a mathematical viewpoint, there are seven basic regimes, of which the known physical regimes are special cases.

KEY WORDS: Crystal growth regimes; asymptotics; polymer crystallization; nucleation; dislocation; Markov process.

1. INTRODUCTION

Mathematical aspects of the growth of two-dimensional crystals, at the molecular level, have been studied by several authors.[17,6,1,12,7-11] This work describes a two-dimensional polymer crystal or a two-dimensional layer on the surface of a three-dimensional crystal or substrate.

Growth regimes are usually described in terms of the model in ref. 6. This represents a crystal edge by a series of one-dimensional layers of unit height in the manner of Fig. 1. Layers are built upon a flat substrate of length L by a process of *nucleation* of new layers and extension of existing layers. A nucleation is an attachment of a particle to a flat layer or an attachment of a new polymer chain. Nucleations are represented by spikes of unit height and are taken to occur independently and uniformly along the edge. They arrive in time as a Poisson process of rate i per unit length. Subsequently, the spikes expand horizontally with speed g in both direc-

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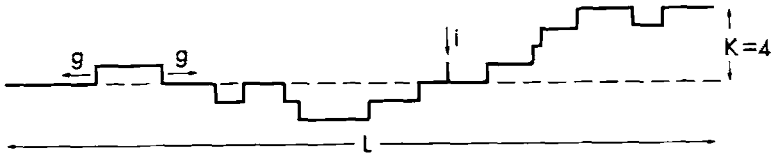

Fig. 1. A crystal edge in a model where steps move with constant horitontal speed g.

tions as new particles or further segments of a polymer chain attach. The growth rate G is the total rate of increase of the area under the edge per unit length.

For a level edge, the steady growth rate takes different forms, depending on ambient conditions:

$$\text{regime I:} \quad G = Li \tag{1.1}$$

$$\text{regime II:} \quad G = (2ig)^{1/2} \tag{1.2}$$

$$\text{regime III:} \quad G = Li/M \tag{1.3}$$

Here M represents the number of particles on the substrate. Polymer scientists have devoted much effort to understanding why such rates are observed and the rather abrupt transitions between regimes that occur as ambient conditions change (see refs. 14, 15, and 18 for reviews). For an inclined edge, with a height difference K between the ends of the substrate, one encounters the formula

$$G = gK/L \tag{1.4}$$

which we call regime IV.

These different regimes have never been derived from a single mathematical model, and that is our purpose here. This enables us to understand the precise mathematical conditions under which various regimes apply and also to elucidate intermediate regimes that connect them. Thus we are able to provide a unification of several partial theories of two-dimensional growth. These include the theory of Bennett *et al.*[1] and Goldenfeld,[12] which gave a more exact version of Frank's theory[6] and yielded regimes I and II; our theory,[8] which unified regimes I, II, and III (called I, IIa, and IIb in ref. 8); and Frank's classical theory[5] of growth driven by dislocations (regime IV).

In the context of Frank's model,[6] regime I is appropriate when

$$L \ll (g/i)^{1/2} \tag{1.5}$$

i.e., the time L/g for a step to traverse the edge is much less than the mean time $1/(Li)$ between nucleations. Then there are typically very few steps on the edge.

Regime III is appropriate when

$$(g/i)^{1/2} \ll L/M \tag{1.6}$$

i.e., looking at one particle site on the edge, the time $M/(Li)$ between nucleations at the site is much less than the time $L/(Mg)$ for a step to advance one particle distance. In this case there are steps at nearly every site, so the edge is very rough. The growth is dominated by nucleation, as (1.3) suggests.

Regime II is appropriate when

$$L/M \ll (g/i)^{1/2} \ll L \tag{1.7}$$

Then there are typically many steps along the edge, but the distance between steps is large.

The formula (1.4) is appropriate at least when $K > 0$ and (1.5) holds. Then the edge typically has exactly K upward steps and no downward steps, leading easily to (1.4). When $K \ll M$, as is usually the case, this regime describes an edge inclined at a small angle $\arctan(K/M)$ to the principal crystal direction. Alternatively it represents a two-dimensional analog of a crystal surface with K screw dislocations, in that the net number of steps is preserved as growth occurs, though their locations can change. When (1.4) applies they dominate the growth process. This phenomenon was postulated long ago by Frank[5] in order to explain why crystals grow much faster than theories based on perfect crystal growth predicted. Now we can give a detailed mathematical description of this phenomenon in two dimensions.

2. THE MODEL AND THE GENERAL GROWTH RATE

Polymers such as poly(4-methylpentene-1) form lamellar crystals in which chain segments pack together in a square array.[16] Looking at the face of such a lamella and viewing a portion of the edge, one sees a stack-like array in which the ends of polymers, which we may represent by squares, form vertical columns as illustrated in Fig. 2a (the so-called *solid-on-solid*, or SOS, model). We invoke periodic boundary conditions. Thus Fig. 2a may be regarded as wrapped around a vertical cylinder so that points A and A' coincide. This implies a K-fold helical structure. As one adds to this structure, the net upward step around one revolution remains fixed at K.

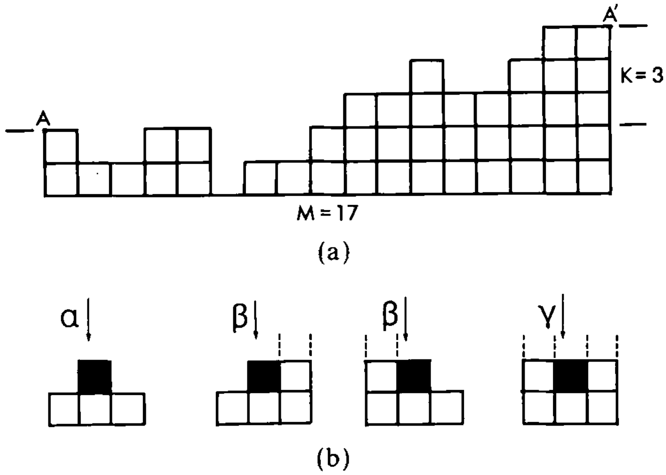

Fig. 2. (a) A crystal edge in the discrete particle Markov model. The pattern continues periodically across, and points A and A' are equivalent. (b) The transitions and their rates.

We are mainly concerned with large M, where the helical structure is unimportant. For small M, however, the grown crystal in our model resembles a helical macromolecule. The analogy between the growth of such molecules and the growth of crystals driven by permanent steps was recognized by Watson (ref. 19, p. 114).

In ref. 7 we also treated crystals with hexagonal structure. Here we confine ouselves to square structure.

Consecutive columns are labeled 1, 2,..., M and the stack may be represented by the vector of occupation numbers $(n_1,..., n_M)$ or heights of columns, or alternatively by the vector of height differences or step sizes $\mathbf{h}=(h_1,..., h_M)$, where $h_j=n_j-n_{j-1}$, where

$$\sum_{i=1}^{M} h_i = K \tag{2.1}$$

Transitions consist of adding one chain segment (or square) to one column, i.e.,

$$h_j \to h_j+1, \qquad h_{j+1} \to h_{j+1}-1 \tag{2.2}$$

for exactly one j. This transition has rate (see Fig. 2b)

$$\begin{aligned} &\alpha && \text{if } h_j \geqslant 0 \text{ and } h_{j+1} \leqslant 0 \\ &\beta=\alpha+\nu && \text{if } h_j \geqslant 0 \text{ and } h_{j+1} > 0, \text{ or } h_j<0 \text{ and } h_{j+1} \leqslant 0 \\ &\gamma=\alpha+2\nu && \text{if } h_j<0 \text{ and } h_{j+1}>0 \end{aligned} \tag{2.3}$$

with α, $\nu > 0$. The three rates correspond to nucleation, to extension of an existing layer, and to joining two portions of a layer, respectively. This is discussed further in ref. 7.

We suppose that the growth is a Markov process in continuous time whose states $\mathbf{h}$ satisfy (2.1) and whose transition structure is governed by (2.2) and (2.3). The state space is countably infinite.

A situation of steady crystal growth corresponds to stationarity of the Markov process. By a slight extension of the argument given in ref. 7 to $K > 0$, the stationary probability distribution is

$$p(\mathbf{h}) = Z^{-1} \exp\left(-2J \sum_{i=1}^{M} |h_i|\right) \tag{2.4}$$

subject to (2.1), where

$$J = \tfrac{1}{4} \log(\gamma/\alpha) \tag{2.5}$$

and Z is the normalizing constant. A convenient base state for the derivation of (2.4) is $\mathbf{h} = (K, 0,..., 0)$ rather than the $\mathbf{h} = \mathbf{0}$ used in ref. 7. We note that Z is the coefficient of z^K in the Laurent series

$$\sum_{\mathbf{h}} z^{\Sigma h_i} \phi^{\Sigma |h_i|} = (1-\phi^2)^M (1-\phi z)^{-M} (1-\phi/z)^{-M} \tag{2.6}$$

where

$$\phi \equiv (\alpha/\gamma)^{1/2} < 1 \tag{2.7}$$

Laurent's integral formula then gives

$$Z = \frac{(1-\phi^2)^M}{2\pi i} \oint_C dz\, z^{-K-1} (1-\phi z)^{-M} (1-\phi/z)^{-M} \tag{2.8}$$

where the closed curve C is confined within the circular annulus

$$\phi < |z| < 1/\phi \tag{2.9}$$

We see from (2.3) that the total rate out of state $\mathbf{h}$ is

$$q(\mathbf{h}) = M\alpha + \nu s(\mathbf{h}) \tag{2.10}$$

where $s(\mathbf{h})$ is the number of $h_i \neq 0$, i.e., the number of steps in the edge. Then the steady growth rate (area per unit length, or particles per site, per unit time) is

$$\begin{aligned} G &= \langle q(\mathbf{h}) \rangle / M \\ &= \alpha + \nu \Pr(h_1 \neq 0) \end{aligned} \tag{2.11}$$

where the expectation $\langle \cdot \rangle$ and the probability are with respect to the distribution (2.4). One easily finds[8]

$$G = \alpha + \nu[1 - Z(M-1)/Z(M)] \tag{2.12}$$

Together with (2.8), this provides an explicit expression for G in terms of M, K, α, and ν. Note that we may write

$$G = \alpha\Gamma(K, S, M) \tag{2.13}$$

where

$$S \equiv (\nu/\alpha)^{1/2} = \{(1-\phi^2)/2\phi^2\}^{1/2} \tag{2.14}$$

which turns out to be a measure of the distance between steps (see Theorem 2 *et seq.*).

Figure 3 shows the dimensionless growth rate $\Gamma = G/\alpha$ plotted against J of Eq. (2.5) for the values $K = 0$, 1, 5, 15, and 50 and for $M = 50$. The curves were computed using the finite sum expression (4.2) for Z in (2.12). The regimes I, II, III, and IV are indicated. The large difference between $K = 0$ and $K > 0$, for ν/α not too small shows the major influence of permanent steps on a moderately smooth edge. The $K = 0$ curve may be compared with Fig. 4 of Hoffman.[15]

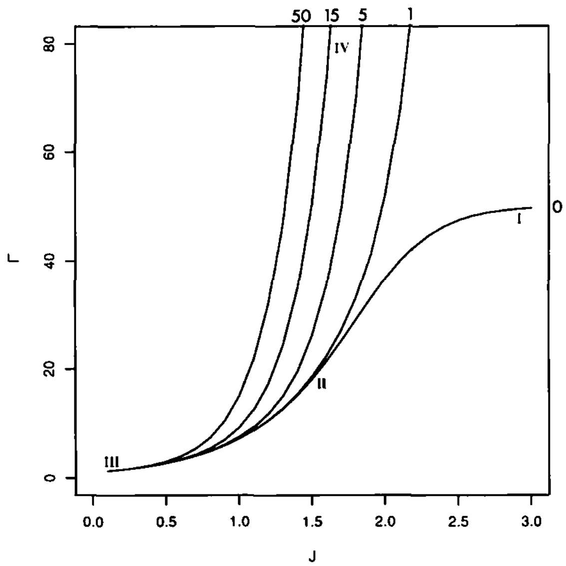

Fig. 3. Plot of the dimensionless growth rate $\Gamma = G/\alpha$ against $J = \frac{1}{4}\log(\gamma/\alpha)$ for $M = 50$ and $K = 0$, 1, 5, 15, and 50. The familiar regimes I–IV are indicated.

Table I. Summary of Regimes when $K>0$

$$K, S, M \begin{cases} KS/M \to 0 \begin{cases} S\to 0\text{: Theorem 3}\\ S>S_0>0\text{: Theorem 2}\end{cases}\\ KS/M \to c \begin{cases} S\to 0\text{: Theorem 3}\\ S>S_0>0 \begin{cases} S\text{ fixed: Theorem 4}\\ S\to\infty\ (K/M\to 0) \begin{cases} M\to\infty,\ K\text{ fixed: Theorem 4}\\ K,\ M\to\infty\text{: Theorem 6}\end{cases}\end{cases}\end{cases}\\ KS/M\to\infty \begin{cases} S\to 0\text{: Theorem 3}\\ S>S_0>0\text{: Theorem 1}\end{cases}\end{cases}$$

We shall also look at the proportion of sites that have steps

$$\zeta(K, S, M) \equiv \langle s(\mathbf{h})\rangle/M = 1 - Z(K, S, M-1)/Z(K, S, M) \qquad (2.15)$$

This provides a simple descriptor of edge roughness that distinguishes among different regimes.

As shown in ref. 8, the discrete SOS model relates to the continuum model of Section 1 as $M\to\infty$, with the identifications

$$M\alpha \to Li \qquad \text{and} \qquad v/M \to g/L \qquad (2.16)$$

Our model involves captures of particles or polymer chain segments by the edge, but not escapes. When crystal growth is slow, escapes become important, and can be incorporated in the model quite easily.[11] The resulting growth rates have a simple multiplying factor, and this does not influence the asymptotic regimes.

The rest of the paper is devoted to a study of various asymptotic regimes defined in terms of the distance parameters K, S, M. The formulas (1.1)–(1.4) are such regimes. The continuum model of Section 1 is itself such a regime. The complete set of regimes is summarized in Table I ($K>0$) and Table II ($K=0$).

Table II. Summary of Regimes when $K=0$

$$0, S, M \begin{cases} S/M\to 0 \begin{cases} S\to 0\text{: Theorem 3}\\ S>S_0>0,\ M\to\infty\text{: Corollary to Theorem 2}\end{cases}\\ S/M\to c\ (S, M\to\infty)\text{: Theorem 5}\\ S/M\to\infty\text{: Theorem 7}\end{cases}$$

Section 3 lists the asymptotic formulas, embodied in Theorems 1–7, and outlines their physical meaning. Section 4 gives various representations of $Z(K, S, M)$ which are used to prove the theorems. The proofs are in Section 5.

3. ASYMPTOTIC FORMULAS AND THEIR PHYSICAL INTERPRETATION

Theorem 1. If $KS/M \to \infty$ and $S \geqslant S_0 > 0$, then

$$\zeta(K, S, M) \sim K/(M+K-1) \tag{3.1}$$

This means that the edge has only those steps forced by the height difference $K > 0$; there are no further steps due to nucleations (α transitions). Here we have a two-dimensional analog of crystal growth driven by screw dislocations. An obvious formula for G follows from (2.12), and for $M \gg K$ it reduces to $G \sim \nu K/M$. The identification (2.16) shows this to be regime IV.

One can also treat this regime as a separate model with $\alpha = 0$. It has statespace with $h_i \geqslant 0$ for all i and with (2.1). The stationary distribution is uniform on this state space, i.e.,

$$p(\mathbf{h}) = Z^{-1}, \qquad Z = \binom{M+K-1}{K} \tag{3.2}$$

which yields (3.1) as an equality.

Theorem 2. If $KS/M \to 0$ and $K > 0$, $S \geqslant S_0 > 0$, then

$$\zeta(K, S, M) \sim 2\phi/(1+\phi) \tag{3.3}$$

Corollary. Result (3.3) holds if $K = 0$, $S/M \to 0$, and $S \geqslant S_0 > 0$.

These results describe the regime opposite to Theorem 1, in which the growth and edge structure are dominated by random captures. Using (2.12) gives the simple formula $G \sim (\alpha\gamma)^{1/2}$. This reduces to $G \sim (2\alpha\nu)^{1/2}$ as $S \to \infty$ and to $G \sim \alpha$ as $S \to 0$. Further terms in an asymptotic expansion are given in ref. 8. With the identification (2.16), we see that we have obtained regimes II and III.

Theorem 3. If $S \to 0$, then $\zeta(K, S, M) \to 1$.

This is more extreme than Theorem 2; now the steps on the edge have *no* influence on the arrival of particles. Thus the stacks grow independently and there is a step at every site. In fact, the Markov process is transient in this case,[7] so steps grow in height without limit. Again $G \sim \alpha$, implying regime III.

Theorems 4–6 deal with the intermediate case $KS/M \to c$, where $0 < c < \infty$. Theorem 2 shows that S is a measure of the mean distance between steps, while M/K is a distance measure for the permanent steps. Thus the breakdown into cases (Table I), dictated by the asymptotic formulas, parallels the breakdown into physically different cases:

(i) $M/K \ll S$, where the permanent steps dominate growth behavior.

(ii) $S \ll M/K$, where the random steps dominate.

(iii) $S \sim M/K$, where both have comparable influence.

Case (iii) is more complex and interesting, and several subcases arise.

Theorem 4. If S is a fixed positive number, M, $K \to \infty$ and $M/K \to D$, where $0 < D < \infty$, then

$$\zeta(K, S, M) \to \frac{1}{D+1} + \frac{D}{D+1} \frac{2\phi}{1-\phi^2} (1 - \phi - s_0^2) \tag{3.4}$$

where s_0^2 is the smaller root of

$$\eta(D-1)\, s^4 - (2 + \eta D)\, s^2 + 1 = 0 \tag{3.5}$$

with $\eta = 4\phi/(1-\phi)^2$.

This provides a useful general formula for a long edge, and contains several of the physically observed rates as special cases.[7] For example, $S \to \infty$ ($\phi \to 0$) gives $\zeta \sim 1/(1+D)$, which is nearly (3.1); and $D \to \infty$ gives $s_0 \to 1$, leading to (3.3) (note, however, that Theorems 1 and 2 do not require a particular limit sequence, and so are more general).

Theorem 5. If K is a (fixed) nonnegative integer and $M/S \to x/\sqrt{2}$, where $0 < x < \infty$, then

$$\zeta(K, S, M) \sim (x/M)\, I'_K(x)/I_K(x) \tag{3.6}$$

where I_K is the modified Bessel function.

This regime is equivalent to the continuum model of Section 1.[7,8] The model was analyzed in its own right by Bennett *et al.*[1] They obtained (3.6) in the case $K = 0$.

Theorems 4 and 5 suggest the complementary limit: fix M and let $KS \to c$. Since $K \to 0$ is meaningless, this leaves only $K \to \infty$, $S \to 0$, which is covered by Theorem 3.

Theorem 6. If K, S, and M all tend to ∞ and $KS/M \to x$, then

$$\zeta(K, S, M) \sim S^{-1}(x^2+1)^{1/2} \tag{3.7}$$

If x is large, this agrees with (3.1); if x is small, it agrees with (3.3). Thus Theorem 6 interpolates in an obvious way between Theorems 1 and 2.

Theorem 7. If $K=0$ and $S/M \to \infty$, then

$$\zeta(K, S, M) \sim (M-1)/S^2 \tag{3.8}$$

This result occupies a slightly special place. From (2.12), $G \sim M\alpha$, meaning that an entire layer is added for each nucleation. The identification (2.16) shows this to be regime I. If there were permanent steps ($K>0$) these would drive the growth, as in Theorem 1. Thus there is a sharp dichotomy between $K=0$ and $K=1$.

The theorems exhaust all the asymptotic formulae for ζ under limiting regimes where parameters or their products or ratios vary monotonically; that is, all the physically sensible regimes. Thus there are only seven different formulas. Tables I and II provide their mathematically natural classification. The physically observed regimes are largely special cases of these.

4. REPRESENTATIONS OF THE BASIC FUNCTIONS

If we choose C in (2.8) to be the unit circle centered at $z=0$, then substituting $z=e^{it}$ produces

$$Z(K, S, M) = (1-\phi^2)^M \frac{1}{\pi}\int_0^\pi dt \frac{\cos Kt}{(1-2\phi\cos t+\phi^2)^M} \tag{4.1}$$

$$= \phi^K \sum_{j=0}^{M-1} \binom{M+K-1}{j+K}\binom{M+j-1}{j}\left(\frac{\phi^2}{1-\phi^2}\right)^j \tag{4.2}$$

[see ref. 13, Eq. (3.616.7)]. It follows from (4.1) that $Z(K, S, M)$ is also proportional to the hypergeometric function $F(M,\ M+K,\ K+1;\ \phi^2)$ [ref. 13, Eq. (9.11.2)] and to the Legendre function $P^K_{M-1}\{(1+\phi^2)/(1-\phi^2)\}$ if $K \leqslant M-1$ [ref. 13, Eq. (8.711.2)]. There are many other possible representations, such as the infinite series for F, but we shall not need these.

The Legendre function leads to a key formula. From ref. 3, §11.62, Examples 2 and 3, it follows easily that, if $K \leqslant M-1$, then

$$Z(K, S, M) = \phi^K (1-\phi^2)^M \frac{2^{2K} K!}{(2K)!} \frac{(M+K-1)!}{(M-1)!}$$

$$\times \frac{1}{\pi} \int_0^\pi dt \frac{\sin^{2K} t}{(1 - 2\phi \cos t + \phi^2)^{M+K}} \tag{4.3}$$

$$= \frac{\phi^K}{(1-\phi)^{2K}} \left(\frac{1+\phi}{1-\phi}\right)^M \frac{2^{2K} K!}{(2K)!} \frac{(M+K-1)!}{(M-1)!}$$

$$\times \frac{2}{\pi} \int_0^{\pi/2} du \frac{\sin^{2K} 2u}{\{1 + 4\phi \sin^2 u/(1-\phi)^2\}^{M+K}} \tag{4.4}$$

The second expression comes from using $\cos t = 1 - 2\sin^2(t/2)$ and setting $u = t/2$. Although this argument requires $K \leqslant M-1$, we have in fact the following result.

Lemma. Equations (4.3) and (4.4) hold for all $K = 0, 1, 2,...$ and $M = 1, 2,...$ and $0 \leqslant \phi < 1$.

This can be proved directly using Jacobi's lemma (see ref. 3, §§11.61 and 11.62). The value of (4.3) and (4.4) lies in the fact they contain non-negative integrands with K always occurring as a power. It follows directly from (2.15) and (4.4) that

$$\zeta(K, S, M) = \frac{K}{M+K-1} + \frac{M-1}{M+K-1} \frac{2\phi}{1-\phi^2} (1 - \phi - 2R) \tag{4.5}$$

where

$$R = \int_0^{\pi/2} du \sin^2 u \; W(u) \Big/ \int_0^{\pi/2} du \; W(u) \tag{4.6}$$

and

$$W(u) = (\sin 2u)^{2K} \Big/ \left\{1 + \frac{4\phi}{(1-\phi)^2} \sin^2 u\right\}^{M+K} \tag{4.7}$$

Thus $0 \leqslant R \leqslant 1$. This shows that the asymptotic behavior of ζ depends on the relative magnitudes of the two terms in (4.5), which effectively means the relative magnitudes of K/M and $\phi = O(S^{-1})$; hence the separation in Table I into cases distinguished by magnitudes of KS/M.

5. PROOFS OF THEOREMS

Proof of Theorem 1. From (4.5)–(4.7), using $0 \leqslant R \leqslant 1$, we find that

$$\frac{K}{M+K-1}\left(1-\frac{2M\phi}{K(1-\phi)}\right) \leqslant \zeta(K, S, M) \leqslant \frac{K}{M+K-1}\left(1+\frac{2M\phi}{K}\right) \tag{5.1}$$

Since $KS/M \to \infty$ is equivalent to $M\phi/K \to 0$, and since $(1-\phi)^{-1}$ is bounded through the condition on S, the theorem follows. The inequality (5.1) provides a more complete statement than the theorem.

Proof of Theorem 2. The second term in (4.5) is dominant under the conditions of the theorem. Hence we require the asymptotic behavior of R in this limit, which is equivalent to $M\phi/K \to \infty$. The method is similar to the Laplace approximation (see ref. 4, Chapter 5). Throughout the proof, $C_1, C_2, \ldots$ are positive constants independent of M, K, or ϕ. For any fixed $\delta > 0$, write

$$\begin{aligned} \int_0^{\pi/2} du\, W(u) &= \int_0^{\delta} du\, W(u) + \int_{\delta}^{\pi/2} du\, W(u) \\ &= I_1 + I_2, \quad \text{say} \end{aligned} \tag{5.2}$$

In I_2, use $\{4\phi/(1-\phi)^2\} \sin^2 u \geqslant 4\phi \sin^2 \delta$, to get

$$\begin{aligned} 0 \leqslant I_2 &\leqslant \exp\{-(M+K) \log(1+4\phi \sin^2 \delta)\} \\ &\leqslant \exp\{-C_1 \sin^2 \delta\, (M+K)\phi\} \end{aligned} \tag{5.3}$$

In I_1, use $(t/\delta) \sin \delta \leqslant \sin t \leqslant t$ $(0 \leqslant t \leqslant \delta)$ and $e^t \geqslant 1+t$ $(t \geqslant 0)$ to get

$$I_1 \geqslant (\delta^{-1} \sin 2\delta)^{2K} \int_0^{\delta} du\, u^{2K} \exp\{-C_2(M+K)\, \phi u^2\} \tag{5.4}$$

Here we are using the condition on S to ensure that $(1-\phi)^{-2}$ remains bounded. Define $\omega = C_2(M+K)\,\phi/K$; clearly $\omega \to \infty$. Then

$$I_1 \geqslant \tfrac{1}{2}(\delta^{-1} \sin 2\delta)^{2K} (\omega K)^{-K-1/2} \int_0^{\delta^2 \omega K} dv\, v^{K-1/2} e^{-v} \tag{5.5}$$

Now use the inequality

$$\int_0^{y} dx\, f(x) \geqslant \int_0^{\infty} dx\, f(x) - \frac{1}{y} \int_0^{\infty} dx\, x f(x) \tag{5.6}$$

for $f \geqslant 0$, which is in effect Markov's inequality (ref. 2, p. 85), to deduce

$$\begin{aligned} I_1 &\geqslant \tfrac{1}{2}(\delta^{-1} \sin 2\delta)^{2K}(\omega K)^{-(K+1/2)}\Gamma(K+1/2)\{1-(K+1/2)/(\omega K)\} \\ &\geqslant C_3(\delta^{-1} \sin 2\delta)^{2K}(\omega K)^{-(K+1/2)}\Gamma(K+1/2) \end{aligned} \tag{5.7}$$

since $\omega \to \infty$. From (5.3) and (5.7), with Stirling's formula for $\Gamma(K+1/2)$, we get

$$0 \leqslant I_2/I_1 \leqslant C_4(\omega K)^{1/2}\{\omega \exp(-C_5 \omega \sin^2 \delta)\delta e/\sin 2\delta\}^K \tag{5.8}$$

So $I_2/I_1 \to 0$ as $\omega \to \infty$, for any $\delta > 0$. Hence, from (4.6),

$$\begin{aligned} 0 \leqslant R &\leqslant (\delta^2 I_1 + I_2)/(I_1 + I_2) \\ &= (\delta^2 + I_2/I_1)/(1 + I_2/I_1) \\ &\to \delta^2 \quad \text{as} \quad \omega \to \infty \end{aligned} \tag{5.9}$$

But δ is arbitrary, so $R \to 0$ as $\omega \to \infty$, i.e., as $KS/M \to \infty$. Rewrite (4.5) as

$$\zeta(K, S, M) = \frac{2\phi}{1+\phi} \frac{M}{M+K-1}\left(1 - \frac{2R}{1-\phi} + \frac{(1+\phi)K}{2M\phi}\right) \tag{5.10}$$

The condition on S implies $K/M \to 0$ and $(1-\phi)^{-1}$ is bounded, and the theorem follows from $R \to 0$. The corollary follows by minor modifications of the argument from (5.4) *et seq.*

Proof of Theorem 3. Use (4.2) with (2.14) to get

$$Z(K, S, M) = \phi^K (2S^2)^{-M+1} \sum_{i=0}^{M-1} b_i(K, M)(2S^2)^i \tag{5.11}$$

where

$$b_i(K, M) = \binom{M+K-1}{i}\binom{2M-2-i}{M-1} \tag{5.12}$$

It is easy to show that $b_i(K, M-1)/b_i(K, M)$ is a decreasing function of i, $0 \leqslant i \leqslant M-2$, so

$$b_i(K, M-1)/b_i(K, M) \leqslant \frac{M-1}{2(2M-3)} \tag{5.13}$$

for such i and for all K and M. Then from (5.11),

$$\begin{aligned} 0 &\leqslant Z(K, S, M-1)/Z(K, S, M) \\ &= 2S^2 \sum_{i=0}^{M-2} b_i(K, M-1)(2S^2)^i \Big/ \sum_{i=0}^{M-1} b_i(K, M)(2S^2)^i \\ &\leqslant 2S^2 \frac{M-1}{2(2M-3)} \end{aligned} \tag{5.14}$$

by (5.13). Hence, for all K, S, M,

$$1 - \frac{M-1}{2M-3} S^2 \leqslant \langle\zeta(K, S, M)\rangle \leqslant 1 \tag{5.15}$$

and the theorem follows easily.

Proof of Theorem 4. Here it is necessary to finds the limit of R. To this end, define $D_K = M/K$ and write

$$\begin{aligned} W(u) &= \{\sin^2 2u/(1+\eta \sin^2 u)^{1+D_K}\}^K \\ &= \{V(u, D_K)\}^K, \quad \text{say} \end{aligned} \tag{5.16}$$

It is easy to show that $V(u, D_K)$ has its maximum at the value of u determined by the smaller solution of (3.5), with D replaced by D_K and $s = \sin u$. Call this solution $s_{0,K}^2 = \sin^2 u_{0,K}$.

We wish to use Laplace's method on both integrals in R, although neither is, at first glance, in exactly the usual form for such an application; in particular, from (5.16) the maximum of the integrand depends on K. But clearly $s_{0,K}^2 \to s_0^2$ as $K \to \infty$, while $V(u, D_K)$, $\sin^2 u$, and their higher derivatives are continuous bounded functions of u. It is then not hard to see from the proof of the Laplace approximation in ref. 4, §18, that essentially the same method proves that

$$\begin{aligned} \int_0^{\pi/2} du\, W(u) &\sim AK^{-1/2}\{V(u_{0,K}, D_K)\}^K \\ \int_0^{\pi/2} du \sin^2 u\, W(u) &\sim AK^{-1/2} s_0^2 \{V(u_{0,K}, D_K)\}^K \end{aligned} \tag{5.17}$$

where A is a constant independent of K. Therefore, from (4.6),

$$R \to s_0^2 \tag{5.18}$$

and the theorem follows from (4.5).

Note that it is not possible to say whether $\int_0^{\pi/2} du\, W(u) \sim AK^{-1/2}\{V(u_0, K)\}^K$, where $s_0 = \sin u_0$, without some assumptions on the rate at which M/K approaches D. Fortunately, this extra result is not needed.

Proof of Theorem 5. The limit $M/S \to x/\sqrt{2}$ is equivalent to $M\phi \to x/2$, by (2.14). In this limit, it is clear from (4.7) that $W(u)$ remains bounded and $W(u) \to (\sin 2u)^{2K} \exp(-2x \sin^2 u)$. So we can apply dominated convergence to both integrals in (4.6) and deduce that

$$R \to \left[\int_0^{\pi/2} du \sin^2 u\,(\sin 2u)^{2K} \exp(-2x \sin^2 u)\right] \times \left[\int_0^{\pi/2} du\,(\sin 2u)^{2K} \exp(-2x \sin^2 u)\right]^{-1}$$
$$= \left[\int_0^{\pi} dt\,(1-\cos t) \sin^{2K} t \exp(x \cos t)\right] \times \left[\int_0^{\pi} dt \sin^{2K} t \exp(x \cos t)\right]^{-1} \qquad (5.19)$$

so

$$1 - 2R \to \{I_K'(x) - (K/x)\, I_K(x)\}/I_K(x) \qquad (5.20)$$

where we have used the integral representation [ref. 13, Eq. (8.431.3)]

$$I_K(x) = \{\Gamma(K+1/2)\sqrt{\pi}\}^{-1}(x/2)^K \int_0^{\pi} dt \sin^{2K} t \exp(x \cos t) \qquad (5.21)$$

But from (4.5),

$$M\zeta(K, S, M) \to K + x \lim(1 - 2R) \qquad (5.22)$$

and the theorem follows from (5.20) and (5.22).

Note that only the case $K > 0$ is compatible with a positive limit for KS/M, but we give the more general result for completeness, since no extra effort is required.

Proof of Theorem 6. We use the notation of the proof of Theorem 4. Then $S/D_K \to x$ and hence $\eta D_K \to 2^{3/2} x^{-1} = \xi$, say. In this limit, the solution $s_{0,K}^2$, which determines the maximum of $V(u, D_K)$, converges to

$$\sigma_0^2 = \{2 + \xi - (4 + \xi^2)^{1/2}\}/(2\xi) \qquad (5.23)$$

Just as in the proof of Theorem 4, we can show that

$$R \to \sigma_0^2 \tag{5.24}$$

Therefore, from (4.5),

$$S\zeta(K, S, M) \to x + \sqrt{2}(1 - 2\sigma_0^2) \tag{5.25}$$

and the theorem follows by simple algebra from (5.23) and (5.25).

Proof of Theorem 7. We see that $S/M \to \infty$ is equivalent to $M\phi \to 0$, which implies that $\phi \to 0$ (excluding $M \to 0$ as trivial). So it is valid to expand $W(u)$ in the binomial series and integrate term by term as required. This easily leads to

$$2R = \frac{1 - 3M\phi + o(M\phi)}{1 - 2M\phi + o(M\phi)} \tag{5.26}$$

so

$$1 - \phi - 2R = (M - 1)\phi + o(M\phi) \tag{5.27}$$

Then, from (4.5),

$$\begin{aligned} \zeta(0, S, M) &= \frac{2\phi}{1 - \phi^2}(M - 1)\,\phi\{1 + o(1)\} \\ &= (M - 1)/S^2\{1 + o(1)\} \end{aligned} \tag{5.28}$$

and the theorem is proved.

Note that it is possible to set up inequalities for ζ in the manner of (5.1), but the details are protracted and unnecessary for our current purpose.

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