

Capture-zone scaling in island nucleation: phenomenological theory of an example of universal fluctuation behavior

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In studies of island nucleation and growth, the distribution of capture zones, essentially proximity cells, can give more insight than island-size distributions. In contrast to the complicated expressions, ad hoc or derived from rate equations, usually used, we find the capture-zone distribution can be described by a simple expression generalizing the Wigner surmise from random matrix theory that accounts for the distribution of spacings in a host of fluctuation phenomena. Furthermore, its single adjustable parameter can be simply related to the critical nucleus of growth models and the substrate dimensionality. We compare with extensive published kinetic Monte Carlo data and limited experimental data. A phenomenological theory sheds light on the result.

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In the active field of statistical mechanics applied to materials, an important unsettled problem in morphological evolution during epitaxial thin film growth [1] is the characterization of the statistical properties of nucleating islands. In particular, for over a decade the universal scaling shape of the island-size distribution (ISD) has been investigated numerically with kinetic Monte Carlo (kMC) simulations, but analytical evaluation has proved elusive. Only rate equations [2, 3, 4] or complicated (often implicit) expressions [5, 6] have been proposed. The ISD is an important tool for experimentalists, since simulations have shown it to be a unique function of the size i of the critical nucleus (see below), a quantity that describes the largest unstable cluster.

A decade ago Blackman and Mulheran [5, 7] proposed subordinating the ISD to the distribution of areas of Voronoi polygons (proximity cells) built around the nucleation centers. Once an island is nucleated, it efficiently captures most of the adatoms diffusing within the capture zone (CZ), a region roughly coinciding with the island's Voronoi polygon. This breakthrough, which invites analogies to distributions of quantum dots [8] and to foams [9], led to several part-numerical, part-analytic investigations [1, 2, 3, 4, 5, 6] that allowed prediction of the ISD for point islands with good accuracy, at the price of performing extensive kMC simulations or of solving a system of several coupled, non-linear rate equations, which is computationally as taxing as kMC. For this reason, an empirical functional form, proposed in Ref. [2], which fits kMC results well, is still widely used to analyze data.

In this Letter, we propose a different approach. We show that the generalized Wigner surmise (GWS) distribution, a class of probability distribution functions rooted in random matrix theory (RMT) [10, 11], yields an excellent quantitative description of the CZ size distributions for all values of the critical nucleus size i in published simulations. Thus, this relatively mature sub-

ject is vitalized and broadened by linkage to universal aspects of fluctuations. RMT experts will find remarkable that the signature exponent has atomistic meaning in these non-equilibrium systems. A phenomenological argument suggests the physical origins of the GWS here.

RMT [10, 11] has been successfully applied as a phenomenological description of statistical fluctuations in a large variety of physical systems, such as highly excited energy levels of atomic nuclei, quantum chaos [12], cross-correlations in financial data [13], stepped crystal surfaces [14], and even times between buses in Cuernavaca [15] and distances between parked cars [16]! The last example is analogous to our study in that the RMT-derived formula accounts for the data notably better than the culmination of years of problem-specific theories.

RMT applies only to matrices with special symmetries, which constrains the applications to physical systems that somehow reflect these symmetry properties.

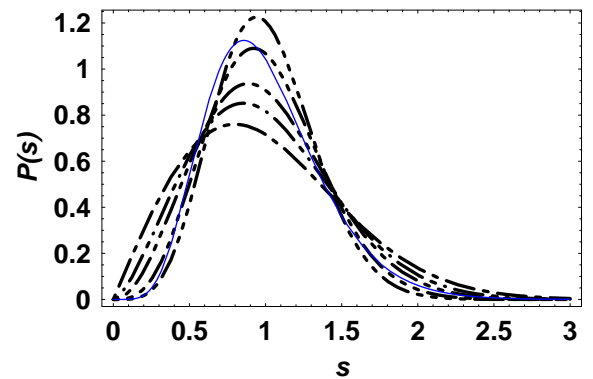


FIG. 1: [Color online] Plots of the GWS of Eq. (1) $P_n(s)$, $n=1,2,3,4$, of relevance in this paper, indicated by long dashes alternating with n short dashes; also $P_{3/2}(s)$, indicated by long dash, short dash, dot. The thin solid [blue] curve shows the Gamma distribution $\Pi_7(s)$, discussed later.

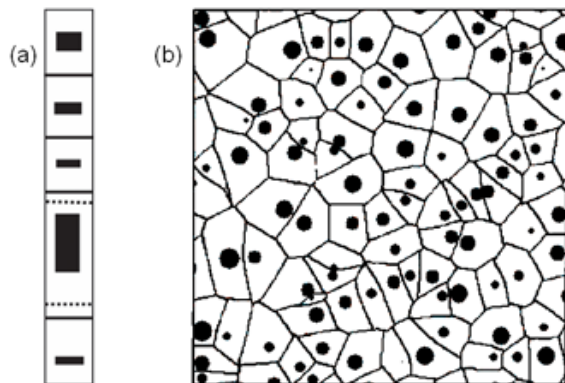


FIG. 2: a) Schematic for 1D (vertical). Black rectangles correspond to 1D islands. Horizontal lines mark the midpoints between the *edges* of two neighboring islands, with the capture zones (CZ) defined as the resulting proximity cells. An alternative definition, implicit in the point-island approximation, uses the midpoint between the *centers* of islands, indicated by dashed lines and leading to Voronoi “cells”. For islands [nearly] the same size, the two [nearly] coincide. b) 2D illustration of the islands (approximated as circular) and the Voronoi polygons that bound their CZ, from Ref. [7].

The Wigner surmise $P_\beta(s)$

$$P_\beta(s) = a_\beta s^\beta \exp(-b_\beta s^2) \quad (1)$$

(cf. Fig. 1) provides a simple, excellent approximation for the distribution of spacings for such cases [10, 11]. Here s is the fluctuating variable divided by its mean, β is the sole WS parameter [17], and a_β and b_β are fixed by the normalization and the unit-mean conditions [18].

Standard RMT [10, 11, 12] fixes attention on the values 1, 2 and 4 of β , corresponding to orthogonal, unitary, and symplectic matrices, respectively. The GWS posits that Eq. (1) has physical relevance for *general* non-negative β [19]. We show here that *the CZ distribution is excellently described by the GWS with $(2/d)(i+1)$* , where $d=1,2$ is the spatial dimension (see Fig. 2). The GWS also describes the distribution of terrace widths on stepped surfaces [14, 19], where the step-repulsion strength determines β .

The explicit dependence of β on dimension is a novel feature of this study. Most other applications of RMT are either essentially one-dimensional or insensitive to d . While $P_1(s)$ describes well the nearest-neighbor spacings between randomly-distributed points on a plane [12], GWS fits of Voronoi tessellations of such points are not particularly good [20, 21]. For island nucleation, subtle correlations between nucleation centers lead to a distribution of tessellation cells (Fig. 2) described by the GWS.

Island nucleation is pictured as atoms deposited on a substrate (at rate F) and then diffusing on the surface at diffusion rate D (most properties depending only on D/F [1]). When adatoms meet, they form bonds, whose lifetime depends on temperature T . At low enough T ,

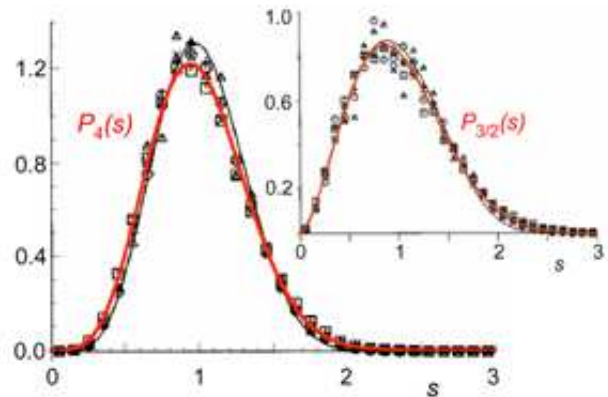


FIG. 3: [Color online] CZ size distributions for critical nucleus size $i=1$ and $d=1$. Symbols are from Fig. 12 of Ref. [5], for various pairs of values of $(D/F$ in units of 10^5 , coverage in monolayers): \square (5, 0.11), \circ (5, 1.19), \triangle (5, 12.65), \times (50, 0.11), $+$ (50, 1.19). The thin curve is the theory prediction of Ref. [5]. The thick [red] curve is the simpler $P_4(s)$. The inset shows similar results for distribution of *gaps* between point islands from Fig. 11 of Ref. [5], with the added thick [red] curve giving $P_{3/2}(s)$; its self-convolution is about $P_4(s)$, the ISD, as discussed near the end.

bonding is virtually irreversible, so that an adatom pair is a stable—and immobile— island, which grows only by capturing other adatoms. A single adatom is then called a *critical nucleus*; equivalently, the critical nucleus size is $i=1$ at low T . At higher T a single bond will be broken before other adatoms can be captured, and the critical nucleus will be a larger cluster, whose size will depend on the surface lattice symmetry, generally $i=2$ or 3 on a (111) or (100) surface, respectively [2, 22].

We first test our approach on data computed by Blackman and Mulheran [5] with kMC simulations of the nucleation of point islands along a one-dimensional (1D) substrate (cf. Fig. 2a). Since $i=1$ there, we predict that the CZ size distribution is a GWS function with $\beta=4$. Fig. 3 shows the results of their simulations, along with fits with the Wigner surmise. Clearly $P_4(s)$ yields an excellent fit to the numerical results, better than the thin solid line, the result [5] of a statistical numerical calculation replacing the solution of a complicated integro-differential equation. Thus, our expression is both more accurate and simpler than their theoretical result.

Two-dimensional (2D) deposition, diffusion, and aggregation models have been extensively treated by many authors. Mulheran and Blackman [7] report kMC simulations of growth of fractal islands ($i=1$) and circular islands ($i=1$ to 3). For the circular islands we find very good agreement between the data and the GWS using $\beta = (2/2)(i+1)$ [23], with the trend for increasing i well reproduced. Even better agreement is found between the GWS $P_{i+1}(s)$ and Mulheran and Robbie’s [6] more recent kMC simulations of nucleation and growth of circu-

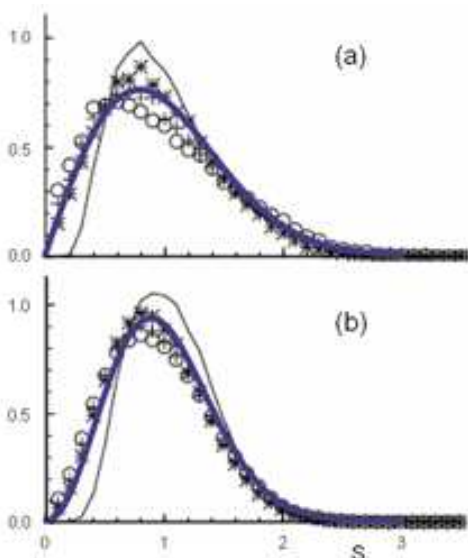


FIG. 4: [Color online] (a) Symbols are numerical data from Fig. 2b of Ref. [6], giving the CZ size distribution for nucleation of islands with $i = 0$ in 2D. The thick (blue) curve is $P_1(s)$. (b) Same as panel (a), but symbols for $i = 1$ from Fig. 2d of Ref. [6], and the thick curve is $P_2(s)$. In both panels the thin curve is the theory of Ref. [6].

lar islands for $i = 0$ and 1, as shown in Fig. 4a and 4b, again superior to their numerical-analytical theory [6]. Popescu et al. [24] also report extensive kMC simulation data of irreversible nucleation ($i = 1$) of point, compact, and fractal islands, but do not compute CZ size distributions. Their rate-equation approach was designed to describe island sizes and capture numbers, so should not, and does not [23], describe the CZ distribution well.

To understand why the CZ distribution is well described by $P_\beta(s)$ with $\beta = (2/d)(i+1)$, we offer a phenomenological model. We draw on our recent demonstration [25] that the GWS appears in the context of RMT as the mean-field solution of Dyson’s Brownian motion model [11, 12], based on a Coulomb gas of logarithmically interacting particles [26] in a 1D quadratic potential well. We argue that the CZ size distribution can be extracted from a Langevin equation for a fluctuating CZ size in a confining potential well created by two competing effects: 1) The effective confining potential well should increase for small-size CZ: nucleation of a new, small island causes a CZ of finite (and not greatly different from the mean) size to appear (cf. Fig. 19 of [27]), so that a large force must prevent fluctuations of the CZ size towards vanishing small values 2) The neighboring CZ’s also prevent the one under scrutiny from growing, exerting a sort of external pressure, which may be assumed to come from a quadratic potential. A noise term represents atoms in a CZ attaching to other than the proximate island.

To compute the repulsion, we analyze quantitatively the nucleation of new islands, following Ref. [28]. If N

is the stable island density, n the adatom density, D the adatom diffusion constant, σ the capture coefficient of an island, and N_i the density of critical nuclei (islands with i atoms), the nucleation rate \dot{N} in 2D is [28]

$$\dot{N} = \sigma n N_i \approx D n^{i+1}. \quad (2)$$

In the rightmost expression we have used $\sigma \approx D$ [28] and the Walton relation $N_i \approx n^i$ [29]. In 2D, n satisfies

$$\dot{n} = F - \sigma n N \approx 0 \Rightarrow n \approx F/(\sigma N) \approx F \ell^2/D \quad (3)$$

where $1/N \approx \ell^2 = D\tau$ is the squared diffusion length of adatoms before capture by an island in lifetime τ . In 1D, Eq. (2) still holds, but accounting for the properties of a random walk in 1D makes the capture coefficient σ dependent on ℓ . Indeed, from [28, 30] we have

$$\dot{N} = \sigma_{1D} n N_i = \frac{n}{\tau} N_i (D\tau)^{1/2} \approx \frac{D}{\ell} n N_i \approx \frac{D}{\ell} n^{i+1}, \quad (4)$$

whence $\sigma_{1D} = D/\ell$. Since $n \propto \ell^2$, regardless of d , and $1/N \approx \ell$ in 1D, Eqs. (2) and (4) can, for $d=1,2$, be written

$$\dot{N} \approx \sigma n^{i+1}, \quad \sigma = D/\ell^{2-d}. \quad (5)$$

Taking the result for \dot{N}/σ in Eq. (5) as a multiplicity, we find an effective entropy $\Sigma = k_B \ln(n^{i+1})$. Identifying $s \equiv \ell^d$ as the “area” in $d=1,2$, and recalling $n \propto \ell^2$

$$(\dot{s})_1 = K \frac{\partial(\Sigma/k_B)}{\partial s} = K \frac{(2/d)(i+1)}{s}, \quad (6)$$

where K is a kinetic coefficient. Fluctuating repulsion (with strength B) from the neighboring CZs yields a second contribution $(\dot{s})_2 = -K B s + \eta$, where η arises from the random component of the external pressure. We arrive at the Langevin equation

$$\dot{s} = K [(2/d)(i+1)/s - B s] + \eta. \quad (7)$$

As we show in Ref. [25], the stationary solution to the Fokker-Planck equation corresponding to Eq. (7) is just the GWS $P_\beta(s)$, with $\beta = (2/d)(i+1)$.

Mulheran and Blackman [7, 31] proposed the Gamma distribution as an empirical description of general Voronoi tessellations, particularly of the CZ size distribution. With unit mean enforced, it has the form [32]

$$\Pi_\alpha(x) = [\alpha^\alpha/\Gamma(\alpha)] x^{\alpha-1} \exp(-\alpha x). \quad (8)$$

No relation was established between the parameter α and any nucleation property, and in accounting for a range of i , a single value of α associated with random deposition is used [7]. The GWS and Gamma distributions are qualitatively similar, and, for $1 \leq \beta \leq 4$, α is roughly $2\beta + \alpha_0$, where α_0 is an offset of order one (cf. $P_3(s)$ and $\Pi_7(s)$ in Fig. (1)); the value of α_0 depends on what property of the two distributions are equated [33]. However, the slower decay of the $\Pi_\alpha(s)$ leads to considerably

greater skewness, with a distinctly greater shift of the peak to smaller s . Like $P_\beta(s)$, $\Pi_\alpha(x)$ approaches a Gaussian for large α . Trying to distinguish the two forms in the large- s tail is problematic since the small values lead to large fractional uncertainty. Very recently $\Pi_\alpha(s)$ has been used as a tool for analyzing experimental CZ distributions [8, 34]. Trial fits of the data with the GWS form are generally at least as good. Amar *et al.*'s popular rate-equation-derived expression for ISD's, noted at the outset, is $f_i(s) \propto s^i \exp(-ia_i s^{1/a_i})$, $i \geq 1$, where a_i is a complicated constant [2]. By construction, it peaks at $s=1$. While not designed for CZ distributions, $f_i(s)$ has been tried as an alternative to $\Pi_\alpha(s)$ for quantum dots, with neither being fully satisfactory [8].

Several extensions and challenges present themselves: 1) We hope experimentalists [8, 34] will refit their data for CZ distributions with the GWS. When Voronoi tessellation is used more generally, e.g. in studying biological systems [35], the resulting size histograms should be analyzed using the GWS and the alternatives. 2) Fig. 2a shows that when there is a wide range of island sizes, using a strict Voronoi construction rather than physically more appropriate edge cells [1, 27] leads to a narrower distribution (hence a higher deduced β). E.g., in fitting numerical data for the irreversible point-island nucleation ($i=1$) in Fig. 3b of Ref. [27], we find much better agreement with $P_4(s)$ than the expected $P_2(s)$. (Other subtleties complicate this case; compact islands occur only at very low coverage (≤ 0.01) [27].) 3) Our predictions should be tested in cases with large i . 4) For $d > 2$, random walks are not recurrent, with the upshot that $\beta=i+1$ as for $d=2$. This can be tested with growth simulations in $d=3$ and $d=4$ [4]. 5) In $d=1$ it is straightforward to find the gap distribution between islands, as done in Ref. 5. The CZ distribution is a self-convolution of the gap distribution [5]. In Fig. 3 we saw $\beta=4$; the gap distribution, then, should be well described by $P_{3/2}(s)$ (viz. $P_4(s) \approx 2 \int_0^{2s} P_{3/2}(s') P_{3/2}(2s-s') ds'$). The inset of Fig. 3 corroborates this. Generalization to $d=2$ is unclear.

In summary, as for spacings between parked cars [16], the Wigner surmise provides a simple, universal expression that accounts better for data than more complicated expressions developed over years of investigation. For our problem of the capture zone distribution in island nucleation, the exponent β of the generalized Wigner surmise $P_\beta(s)$ provides information about the size i of the critical nucleus and reflects the dimensionality d . Our phenomenological argument provides insight into the physical origin of this behavior. Both features are significant advances beyond previous empirical analytic descriptions of the CZ size distribution (notably $\Pi_\alpha(x)$). The connection to universal properties of fluctuations enhances the interest and importance of studies of CZ distributions and suggests many avenues for further investigations.

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