

Capture-Zone Scaling in Island Nucleation: Universal Fluctuation Behavior

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In island nucleation and growth, the distribution of capture zones (in essence proximity cells) can be described by a simple expression generalizing the Wigner surmise (power-law rise, Gaussian decay) from random matrix theory that accounts for spacing distributions in a host of fluctuation phenomena. Its single adjustable parameter, the power-law exponent, 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 elucidates 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 characterizing the statistical properties of nucleating islands. The island-size distribution (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. In particular, for over a decade the universal scaling shape of the ISD has been investigated numerically with kinetic Monte Carlo (KMC) simulations, but analytical evaluation has proved elusive. Only rate equations [2,3] or complicated (often implicit) expressions [4,5] have been proposed.

A decade ago Mulheran and Blackman (MB) [4,6] proposed subordinating the ISD to the distribution of areas of Voronoi polygons (proximity—generalized Wigner-Seitz—cells) built around the nucleation centers. Once an island is nucleated, it efficiently captures most of the adatoms diffusing within the capture zone (CZ), which coincides roughly with its Voronoi polygon. This breakthrough led to several investigations [1,3,5] that allowed accurate prediction of the ISD for point islands, at the price of performing extensive KMC simulations or of solving a system of several coupled, nonlinear rate equations, which is computationally as taxing as KMC. Hence, an empirical functional form, proposed in Ref. [2], which fits KMC results well, is still widely used to analyze data.

Since a gamma distribution describes the area distribution of a two-dimensional (2D) random Voronoi network [7], MB [6,8] proposed it as an alternative description for CZ distributions. The characteristic exponent [called α in Eq. (6)] perforce increases from ~ 3.6 —the point-island limit—dramatically (in an ill-defined way) as exclusion is included [6], but with no succinct interpretation.

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) [9,10], 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 subject can be related to universal aspects of fluctuations. RMT savants will find it remarkable that the signature exponent has atomistic meaning in these nonequilibrium systems. A phenomenological argument suggests the physical origins of the GWS description.

RMT [9,10] successfully describes the fluctuations of spacings in manifold physical systems, e.g., highly excited energy levels of atomic nuclei, quantum chaos [11], cross correlations in financial data [12], stepped crystal surfaces [13], and even arrival time intervals between successive buses in Cuernavaca [14] and distances between parked cars [15]. The last example is analogous to our study: the RMT-derived formula accounts for the data—in a system with irreversible dynamics—at least as well as, usually better than, more complicated *ad hoc* expressions developed over many years.

RMT applies to systems with special symmetries, represented by orthogonal, unitary, or symplectic matrices. For such cases, the Wigner surmise (WS) $P_\beta(s)$,

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

(cf. Fig. 1) provides a simple, excellent approximation for the distribution of spacings [9,10]. Here s is the fluctuating variable divided by its mean, and β is the sole WS parameter [16]—taking the values 1, 2, or 4, respectively. The constants a_β and b_β are fixed by the normalization and the unit-mean conditions, respectively [17].

The GWS posits that Eq. (1) has physical relevance for systems not manifesting these symmetries, so having *general* non-negative β [18], as in Dyson's Coulomb-gas model [19(a)] or the Calogero-Sutherland model of one-dimensional (1D) fermions [19(b)–19(e)]. We show here that the CZ distribution is excellently described by the GWS with $\beta = (2/d)(i + 1)$, where $d = 1, 2$ is the spatial dimension (see Fig. 2). The GWS also describes the distribution of terrace widths on stepped surfaces [13,18], where the step-repulsion strength determines β . As in that case, the significance of applicability of the GWS is

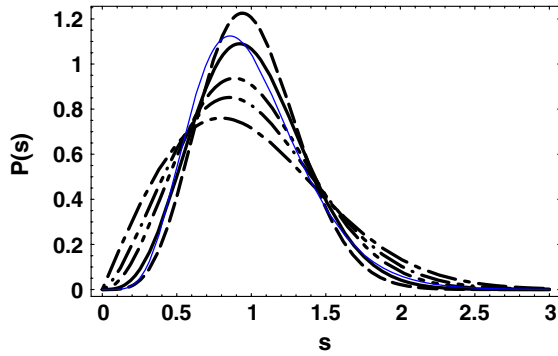


FIG. 1 (color online). Plots of the GWS of Eq. (1) $P_n(s)$, $n = 1, 2, 3, 4$, of relevance in this Letter, indicated by long dashes alternating with n short dashes, also $P_{3/2}(s)$, indicated by the long dashed, short dashed, dotted curve. The thin (blue) solid curve shows the gamma distribution $\Pi_7(s)$, discussed later.

not so much the usually improved fit of data, but rather the greater insight obtained.

The explicit dependence of β on dimension is a novel feature of this study. Most other applications of RMT are either essentially 1D or insensitive to d . While $P_1(s)$ describes well the nearest-neighbor spacings between randomly distributed points on a plane [11], GWS fits of Voronoi tessellations of such points are not particularly good [22,23]. 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

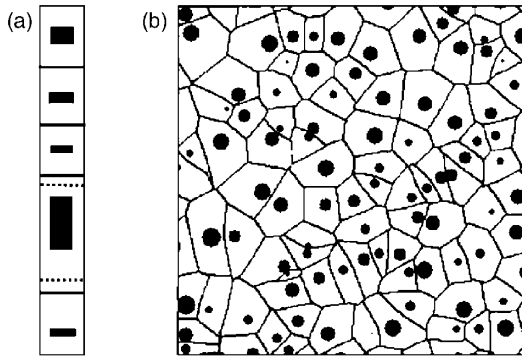


FIG. 2. (a) Schematic for 1D (vertical). Black rectangles correspond to 1D islands. Horizontal lines mark the midpoints between the *edges* of two neighboring islands, with the CZs defined as the resulting proximity cells (edge cells [1,20]). An alternative definition, implicit in the point-island approximation, 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; otherwise, edge cells have a narrower distribution [21]. (b) 2D illustration of the islands (approximated as circular) and the Voronoi polygons that bound their CZ, from Ref. [6(b)].

depends on temperature T . At low enough T , 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, so 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 [2,24].

We first test our approach on data computed by Blackman and Mulheran [4] with KMC simulations of the nucleation of point islands on a 1D substrate [cf. Fig. 2(a)]. Since $i = 1$ then, we predict that the CZ size distribution has the GWS form with $\beta = 4$. Figure 3 shows the results of their simulations, along with two curves. The simple expression $P_4(s)$ accounts arguably at least as well for the numerical data as the thin solid line, from their statistical numerical calculation replacing the solution of a complicated integro-differential equation.

Many authors have treated 2D deposition, diffusion, and aggregation models extensively. MB [6] 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 $\beta = (2/2)(i + 1)$ [25(a)], 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 [5] more recent KMC simulations of nucleation and growth of circular islands for $i = 0$ and 1 , as shown in Figs. 4(a) and 4(b), again superior to their numerical-analytical theory [5].

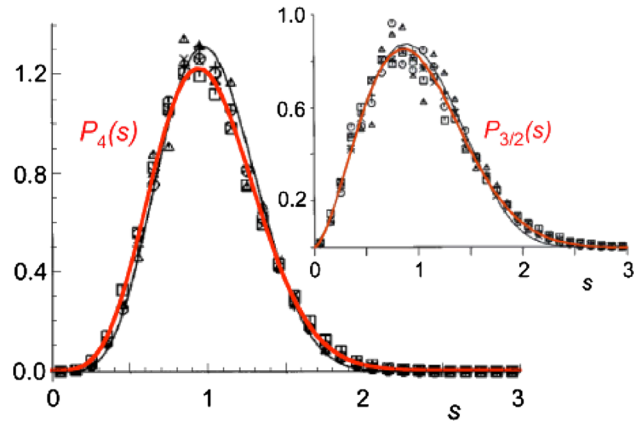


FIG. 3 (color online). CZ size distributions for critical-nucleus sizes $i = 1$ and $d = 1$. Symbols are from Fig. 12 of Ref. [4], for various pairs of values of $(D/F$ in units of 10^5 , coverage in monolayers) \square (5, 0.11), \odot (5, 1.19), \triangle (5, 12.65), \times (50, 0.11), $+$ (50, 1.19). The thin curve is the theory prediction (requiring an integration and fitting a free parameter) of Ref. [4]. 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. [4], with the added thick (red) curve giving $P_{3/2}(s)$; its self-convolution [4] [viz. $2 \int_0^{2s} P_{3/2}(s')P_{3/2}(2s - s')ds'$] $\approx P_4(s)$, the CZ distribution. Generalization to $d = 2$ is unclear.

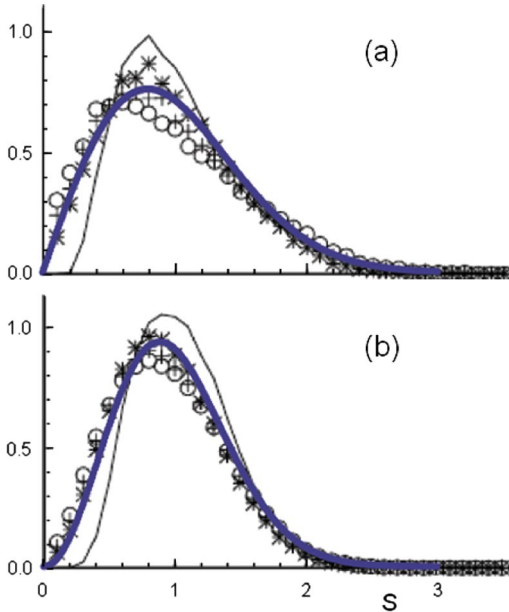


FIG. 4 (color online). (a) Symbols are numerical data from Fig. 2(b) of Ref. [5], giving the CZ size distribution for nucleation of islands with $i = 0$ in 2D. The thick (blue) curve is $P_1(s)$. (b) Same as panel (a), but symbols for $i = 1$ are from Fig. 2(d) of Ref. [5], and the thick curve is $P_2(s)$. In both panels the thin curve is the theory of Ref. [5].

Popescu *et al.* [26] 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 it should not, and does not [25], 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 [27] that the GWS appears in the context of RMT as the mean-field solution of Dyson's Brownian motion model [10,11], based on a Coulomb gas of logarithmically interacting particles [28] 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 local mean—size to appear (cf. Fig. 19 of [20]), so that a large force must prevent fluctuations of the CZ size toward vanishingly small values. As i increases, the chance of finding a very small CZ should decrease. (2) The neighboring CZs 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.

More formally, we argue that the CZ distribution can be described by a Fokker-Planck equation that has the GWS $P_\beta(s)$ [27], with $\beta = (2/d)(i + 1)$, as its stationary solu-

tion. That equation is associated with the Langevin equation, for $d = 1, 2$ [29],

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

where K is a kinetic coefficient. The fluctuating repulsion (with strength B) from the neighboring CZs yields a contribution to (\dot{s}) of $-KBs + \eta$, where η arises from the random component of the external pressure.

To rationalize the $(2/d)(i + 1)/s$ repulsion, we analyze quantitatively the nucleation of new islands, following Ref. [30]. 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 and assuming unit lattice spacing, is [30]

$$\dot{N} = \sigma n N_i \approx D n^{i+1}. \quad (3)$$

In the rightmost expression we have used $\sigma \approx D$ [30] and the Walton relation $N_i \approx n^i$ [31]. The exponent $i + 1$ leads to the strength of the s^{-1} repulsion.

One approach [25,29] argues phenomenologically that there is an effective entropy $k_B \ln(n^{i+1})$ whose derivative with respect to s leads to the repulsive term in Eq. (2). Instead, we here take the inverse approach, perhaps more convincing, of showing that the CZ distribution should be $\propto s^{(2/d)(i+1)}$ for small s and that the repulsion thus must have the claimed strength. If we consider the analogue of Eq. (3) for each capture-zone area A ($s \equiv A/\langle A \rangle$), then

$$\dot{N}(A) \approx D n^{i+1} P(s). \quad (4)$$

We also note that nucleation of an island with CZ of order A takes place in a region where the neighboring CZs have a similar size, especially for small CZs, $A \ll \langle A \rangle$. As the mean adatom density \bar{n} is the solution of a deposition/diffusion equation, $\bar{n} \sim \ell^2$ in a region of linear size ℓ (independent of d) [32]. Thus, $\bar{n}(A)$ is $nA/\langle A \rangle$, and

$$\dot{N}(A) \approx D \bar{n}^{(i+1)} \approx D (nA/\langle A \rangle)^{(i+1)}. \quad (5)$$

Comparing, we have the desired result $P(s) \approx s^{(i+1)}$. For $d = 1$, where the CZs are line segments, we can make a similar argument, but the local mean adatom density is now $\bar{n}(A) \approx n(A/\langle A \rangle)^2$; hence, $P(s) \approx s^{2(i+1)}$.

The GWS is qualitatively similar to MB's [6,8] semi-empirically [33] proposed gamma distribution, explicitly (with unit mean enforced)

$$\Pi_\alpha(s) = [\alpha^\alpha / \Gamma(\alpha)] s^{\alpha-1} \exp(-\alpha s). \quad (6)$$

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 $P_\beta(s)$ and $\Pi_\alpha(s)$ is equated [34]. 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 $e^{-\alpha s}$ from $e^{-\beta s^2}$ decay is problematic due to the large fractional uncertainty. Also, modifying our Fokker-

Planck argument [27] to produce $\Pi_\alpha(s)$ rather than $P_\beta(s)$ as the stationary solution (e.g., by replacing in Eq. (2) KBs with a constraining force independent of CZ size s) essentially eliminates proper correlations between fluctuating CZs. Arguably the main advantage of the GWS is that β identifies the critical-nucleus size i and connects to the extensive work on fluctuations.

Very recently $\Pi_\alpha(s)$ has been used as a tool for analyzing experimental CZ distributions [35,36]. Our trial fits of the data with the GWS form are generally at least as good; moreover, the extracted value of i is plausible. 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 [36(b)]. Voronoi tessellation has also been applied to studying biological systems, e.g., lipid-bilayer head groups [37].

In summary, as for spacings between parked cars [15], 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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