

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, it has been recognized that study of the distribution of capture zones (CZ), essentially proximity cells, may provide more insight than the more-usual investigations of island-size distributions. In contrast to the complicated expressions, ad hoc and derived from rate equations, that have been used, we find that the CZ distribution can be described by simple expression generalizing the Wigner surmise from random matrix theory that describes the joint probability function of a host of fluctuation phenomena. We further show that the characteristic exponent β in this expression is $i + d/2$, where i is the critical nucleus of growth models and d is the dimensionality. We compare with extensive published kinetic Monte Carlo data and limited experimental data. We present of phenomenological theory to justify the result.

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An important open problem of statistical mechanics applied to materials science is the computation of the statistical properties of nucleating islands on a solid surface. In particular, for more than a decade the universal scaling shape of the distribution of the island sizes (ISD) has been investigated numerically with kinetic Monte Carlo (kMC) simulations, analytical evaluation has proved elusive. Only simple rate equations or complicated (often implicit) expressions 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 by Blackman and Mulheran [1] proposed subordinating the ISD to the distribution of areas of Voronoi polygons (proximity cells) built around the nucleation centers. In fact, once an island is nucleated, it captures very efficiently most of the adatoms diffusing within a region, called the capture zone (CZ), roughly coinciding with the island's Voronoi polygon. This breakthrough led to several part-numerical, part-analytic investigations REF that allowed one to predict 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 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 experimental data. Furthermore, even though the CZ size distribution seems to contain more fundamental physics than the ISD, theoretical effort REF has focussed on the latter.

In the present Letter, we propose a different approach. We first show that a class of probability distribution functions known as the generalized Wigner surmise (GWS), rooted in Random Matrix Theory (RMT) [3, 4], yields an excellent quantitative description of the CZ size distributions for all values of the nucleus size i for which

simulations data have been published. We then justify this result with a phenomenological argument.

The relation to universal aspects of fluctuations is particularly exciting. RMT [3, 4] 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 [5], and stepped crystal surfaces [6]. Complex, non-hermitian random matrices have been also studied [7, 8]; applications have yielded a universal model for the fluctuations of dissipative quantum systems [5] and a model of two-dimensional (2D) space-filling random cellular structures [9]. RMT considers only with matrices with special symmetries, which constrains the applications to physical systems that somehow reflect these symmetry properties. The Wigner surmise provides a simple, excellent approximation for the joint probability distribution for such cases. The GWS extends the result by allowing the key parameter in the expression to take on general values. This generalization is crucial for our description of CZ distributions in island nucleation.

We first synopsise island nucleation. When atoms are deposited on a substrate (at a rate F , usually measured in monolayers per second (ML/s)), they diffuse on the surface at a diffusion rate D (measured in squared neighbor spacings per second). When they meet, adatoms form bonds, whose lifetime 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. It is then said that a single adatom is a critical nucleus, or equivalently that 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, 11].

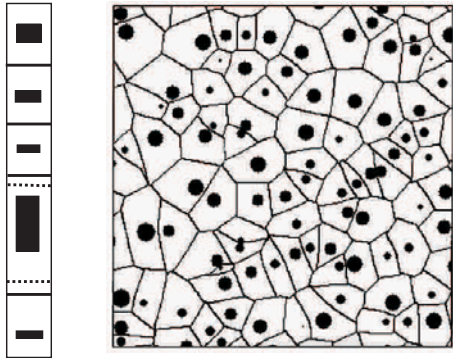


FIG. 1: (a) Schematic of the model in 1D (vertical). The rectangles correspond to the islands; the midpoints between the edges of two neighboring islands are indicated by horizontal lines, with the capture zones (CZ) defined as the resulting proximity cells. In an alternative definition, such as arises in the point-island approximation, the midpoint of the distance between the centers of islands, indicated by dashed lines and the 1D equivalent of Voronoi polygons, is used. For islands nearly the same size, the two coincide. (b) 2D illustration of the islands (approximated as circular) and the Voronoi polygons (proximity cells) that bound their CZ, from Ref. [10].

Before examining published kMC data REF, we recall that the Wigner surmise has the functional form [3, 4]:

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

where s is the fluctuating variable divided by its mean, β is the sole WS parameter [12], and the coefficients a_{β} and b_{β} are fixed by the normalization and the unit-mean conditions:

$$a_{\beta} = 2 \frac{\Gamma\left(\frac{\beta+2}{2}\right)^{\beta+1}}{\Gamma\left(\frac{\beta+1}{2}\right)^{\beta+2}} \quad b_{\beta} = \frac{\Gamma\left(\frac{\beta+2}{2}\right)^2}{\Gamma\left(\frac{\beta+1}{2}\right)^2}. \quad (2)$$

Standard RMT [3, 4, 5] fixes attention on the values 1, 2 and 4 of β , corresponding to orthogonal, unitary, and symplectic matrices, respectively. The WS is an outstanding approximation of the joint probability distribution describing the statistics of fluctuations of the eigenvalues of these random matrices. The *generalized* Wigner surmise (GWS) posits that Eq. (1) has physical relevance for *arbitrary* non-negative β [13]. We show here that *the CZ distribution is excellently described by the GWS with $\beta = i + d/2$* , where d is the spatial dimension. If nucleation were to take place on a fractal substrate [14], non-rational values of β could occur. This feature also appears in another problem of surface physics, viz. the distribution of terrace widths on vicinal surfaces [6, 13].

Note that the GWS can be written in terms of a Gamma distribution for the variable $x = (b_{\beta}/\alpha)s^2$:

$$\Pi_{\alpha}(x) = [\alpha^{\alpha}/\Gamma(\alpha)] x^{\alpha-1} \exp(-\alpha x), \quad (3)$$

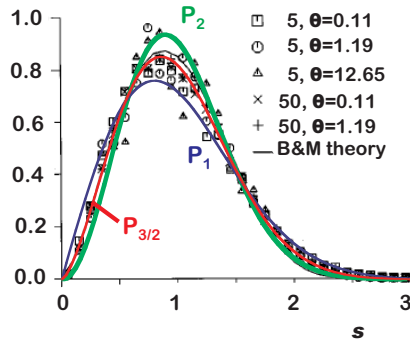


FIG. 2: [Color online] Symbols are from Fig. 11 of Ref. [1]. The critical nucleus size $i=1$ and $d=1$. The first number for each symbol is D/F in units of 10^5 while the second is the coverage in monolayers. The thin solid line denoted “theory” is the prediction of Ref. [1]. The curves are plots of the GWS with $\beta = 1$ (dashed, blue), $\beta = 3/2$ (solid, red), and 2 (dot-dashed, green).

identifying $\beta = 2\alpha - 1$. Interestingly, a Gamma distribution has been proposed [10] as an empirical description of general Voronoi tessellations, and in particular of the CZ size distribution. Very recently $\Pi_{\alpha}(x)$ has been used as a tool for analyzing CZ distributions [15]. However, no relation was established between the parameter α or β of the distribution and any nucleation property. Here we show that fitting measured (or computed) CZ distributions to our GWS functional form allows one to derive information about the critical-nucleus size i . To test the validity of our approach, we proceed to compare our analytic GWS prediction with simulation data available in the literature.

We first test our approach on data computed by Blackman and Mulheran [1] with kMC simulations of the nucleation of point islands along a one-dimensional (1D) substrate. Since $i=1$ in this study, we predict that the CZ size distribution is a GWS function with $\beta = 1 + 1/2$. Fig. 2 shows the results of their simulations for the distribution of gaps between point islands, along with fits with the Wigner surmise. Clearly $P_{3/2}(s)$ yields an excellent fit to the numerical results, better than the theory of Ref. [1], which yields the thin solid line. That theory is the result of a statistical numerical calculation replacing the solution of a complicated integro-differential equation. The usefulness of such a good approximation by our analytical result is obvious.

Two-dimensional (2D) deposition, diffusion, and aggregation models have been extensively treated by many authors. Mulheran and Blackman [10] 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 $\beta = i + 2/2$, as shown in Fig. 3a, with the trend for

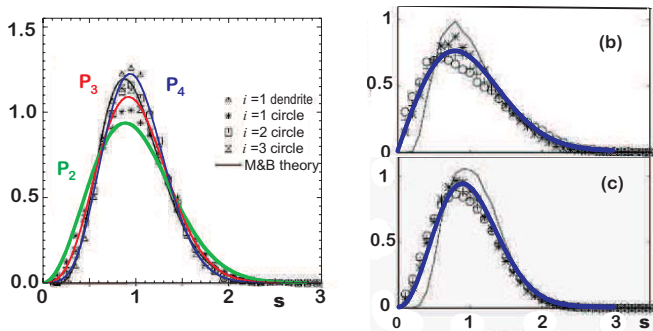


FIG. 3: [Color online] (a) Symbols are numerical data from Fig. 9 of Ref. [10], giving the CZ size distribution for circular islands with $i=1, 2$ and 3 , and for fractal islands (dendrites, $i=1$). The solid curves are GWS function with $\beta=2$ (green), $\beta=3$ (red) and $\beta=4$ (blue). The thin black curve is a Gamma function (in s) with $\alpha \simeq 8$. (b) Symbols are numerical data from Fig. 2b of Ref. [16], giving the CZ size distribution for nucleation of islands with $i=0$ in 2D. The solid (blue) curve is $P_1(s)$. (c) Same as panel (b), but symbols for $i=1$ from Fig. 2d of Ref. [16], and the solid curve is $P_2(s)$. In panels (b) and (c), the thin solid line is the theory of Ref. [16].

increasing i well reproduced. Even better agreement is found between the GWS and Mulheran and Robbie’s [16] more recent kMC simulations of nucleation and growth of circular islands for $i=0$ and 1 , as shown in Fig. 3b and 3c. Indeed, the agreement with $P_{i+1}(s)$ is superior to that with their numerical-analytical theory [16].

Although $P_2(s)$ does not well describe the CZ distribution of fractal ($i=1$) islands [17] in Fig. 3a, this may well be due to the high coverage ($\theta = 0.25$), at which significant coalescence has already taken place (cf. Fig. 1 of Ref. [10]). Judging from Fig. 3 of Ref. [10], $P_2(s)$ is more descriptive of low-coverage ($\theta = 0.05$) data.

Popescu et al. [18] also report extensive kMC simulation data of irreversible nucleation ($i=1$) of point, compact, and fractal islands. The authors do not compute any CZ size distributions in their simulations. However, using a rate-equation approach they extract from their numerical results a prediction of the CZ distribution for compact islands, shown in Fig. 4a as a thin solid line. For comparison, in the original figure data points taken from Ref. [16] were plotted. Using a thick black line, we superimpose $P_2(s)$, which evidently agrees much better with the data than the theory of Ref. [18].

From Evans and Bartelt’s extensive work [19] on irreversible point island nucleation, Fig. 4b shows their computed CZ size distribution. Even though $i=1$ in this work, the CZ size distribution does not agree with that for compact islands from Refs. [10, 16]. However, the data are still extremely closely reproduced by $P_4(s)$, corresponding to $i=3$. While the reason for this is unclear, the irreversible aggregation ($i=1$) is the most complex case, and point island simulation may only be compared with compact islands at very low coverage (≤ 0.01) [19]. Further, as shown in Fig. 1a, using the point-island ap-

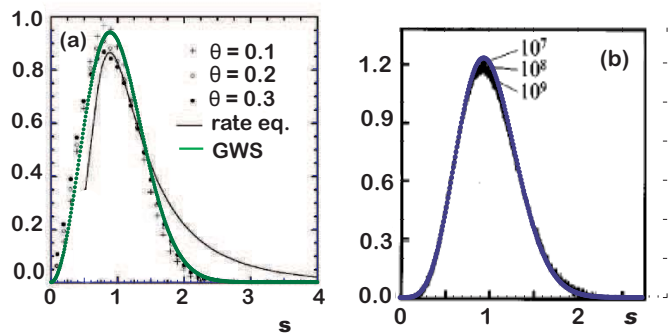


FIG. 4: [Color online] (a) Symbols are kinetic Monte Carlo simulation data for compact islands with $i=1$ taken from Fig. 9 of Ref. [18], which in turn took them from Ref. [16]. The thick green line is $P_2(s)$ (cf. Fig. 3b.). The thin line is the rate-equation theory of Ref. [18]. (b) Curves are CZ size distributions taken from Fig. 3b of Ref. [19]. The thick (blue) line, almost indistinguishable from the data, is $P_4(s)$.

proximation when there is a wide range of island sizes leads to a narrower distribution (effectively higher β) of estimated CZ sizes.

Lest we leave the impression that the GWS is a panacea, we note that GWS fits of Voronoi tessellations of randomly distributed points in 2D are not particularly good [9, 20].

Finally, we provide a phenomenological model for the distribution of CZ sizes for islands in dimension d . We argue that the CZ size distribution can be extracted from a Langevin equation for a fluctuating CZ, embedded in a “mean field” created by neighboring CZs. We have recently [21] shown that the GWS appears in the context of RMT as the mean-field solution of a Brownian motion model [4, 5]. Specifically, Dyson derived a model of a Coulomb gas of logarithmically interacting particles on a line, performing a random walk in a quadratic potential well. Our mean-field version of the corresponding Langevin equation is associated with a Fokker-Planck equation whose stationary solution is $P_\beta(s)$ [21]. Note Ginibre’s extension to $d=2$ of Dyson’s model [7].

The excellent agreement between the GWS with $\beta = i + d/2$ and the variety of simulation data may be understood by viewing the CZ as performing a random walk in a confining potential well due to two competing effects: 1) The neighboring CZs prevent the one under scrutiny from growing, exerting a sort of external pressure, which may be assumed to come from a quadratic potential. There is also a noise term consistent with atoms in a CZ attaching to other than the proximate island. 2) The effective confining potential well should also increase for small-size CZ: nucleation of a new island causes a CZ of finite (and not greatly different from the mean) size to appear [22], so that a large force must prevent fluctuations of the CZ size towards vanishing small values. In Dyson’s

model this large force comes from a logarithmic interaction potential, yielding a repulsive force diverging with separation r as $1/r$.

We argue that a logarithmic *effective* potential is present in the Langevin equation for the CZ size, due to entropic (steric) repulsion. To compute it we must analyze nucleation of new islands. We use the results of Ref. [23] to treat nucleation in $d = 1$ and 2 spatial dimensions. If N is the stable island density, n the adatom density, and N_i the density of critical nuclei (islands of size i atoms), the nucleation rate may be written as

$$\dot{N} = (n/\tau) N_i (D\tau)^{d/2}, \quad (4)$$

where τ is the typical lifetime of a diffusing adatom before being captured by an island, and D its diffusion constant. The factor $(D\tau)^{d/2}$ is the number of distinct sites visited by the adatom during its lifetime. In this relation, n/τ is the rate of disappearance of adatoms, while $N_i (D\tau)^{d/2}$ is proportional to the probability of finding a critical nucleus. Defining an effective entropy $\Sigma = -k_B T \ln[N_i (D\tau)^{d/2}]$, we have the repulsive contribution to the Langevin equation:

$$(\dot{s})_1 = -K\partial(\Sigma/k_B T)/\partial s = K\partial \ln [N_i (D\tau)^{d/2}]/\partial s. \quad (5)$$

The effective entropy is a function of s because the nucleus density is given by a Walton relation $N_i \approx n^i$ [24], and the adatom density is proportional to the CZ area, $n \propto s$. Also, the number of sites visited during the adatom lifetime is of order $D\tau \propto s$. Hence,

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

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

$$\dot{s} = K \left[\frac{i + d/2}{s} - Bs \right] + \eta. \quad (7)$$

As we show in Ref. [21], the stationary solution to the corresponding Fokker-Planck equation is just the GWS $P_\beta(s)$, with $\beta = i + d/2$.

In conclusion, we have shown that the generalized Wigner surmise provides an excellent description of the capture zone distribution in island nucleation. We have explained the agreement with a phenomenological argument that links the capture zone size distribution with random matrix theory, and thus opens up new interesting fields of investigation. We stress that contrary to previous empirical analytic description of the CZ size distribution (notably the Gamma distribution $\Pi_\alpha(x)$ which—like $P_\beta(s)$ —approaches a Gaussian for large α), the Wigner surmise allows one to determine the size i of the critical nucleus from a comparison with experimental data.

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