Materials Physics and Mechanics 21 (2014) 207-221 Received: September 18, 2014

SIZE DISTRIBUTIONS AND SCALING IN HETEROGENEOUS NUCLEATION WITH SIZE-LINEAR RATE CONSTANTS

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Abstract. We present a theoretical analysis of rate equations for heterogeneous nucleation of nanomaterials with linear size dependences of the aggregation and fragmentation rate constants. Two scenarios are considered, one relating to stable growth and the other describing unstable situation with a time-dependent critical size. An interesting analytical solution is obtained which is exact in the stable case and only asymptotic in the unstable growth. This solution is expressed through the Polya distribution. Its continuum form features scaling properties for all but very small sizes, which is an intrinsic property of the model. Our scaled size distribution is capable of reproducing both monomodal and monotonically decreasing shapes depending on the value of the dimerization constant. The obtained solution is shown to reproduce fairly well some experimental size spectra of linear chains of metal adatoms on Si(100) surfaces.

1. Introduction

Theoretical analysis of the size distributions (SDs) of different "clusters" (droplets, nanopores, surface islands, nanowires, linear rows) is paramount from the fundamental viewpoint as well as for controlling physical and mechanical properties of nanomaterials. Nucleation of clusters from a metastable mother phase (supersaturated three-dimensional vapor or two-dimensional "sea" of adatoms) can occur either homogeneously, i.e. with all the clusters consisting of only one type of "monomers", or heterogeneously, where the clusters form on a foreign nucleation centers (charged ions, impurities, surface defects *etc*.). In two-dimensional systems such as solid surfaces at submonolayer coverage, new adatoms are continuously brought to the system from a vapor flux. At very high degree of supersaturation of a mother phase (for example, for surface layers at a low temperature), the critical size of classical nucleation theory approaches one and the entire growth process proceeds almost irreversibly before the coalescence stage. In this case, the rate equations (REs) for completely irreversible growth or irreversible growth above a specified and time-independent critical size can be applied [1-21], with the effective capture coefficients (more generally – rate constants) depending on the cluster size and coverage. At lower supersaturations, decay of clusters becomes important and should be accounted for in the corresponding REs, as in classical nucleation theory [22-26]. Discrete REs comprise infinite set of the connected non-linear differential equations. Consequently, despite the important inputs from mathematical community (see, e.g., Refs. [27, 28]), the exactly solvable cases [4, 15, 29-31] are rare.

One of the most interesting properties of these REs (usually considered in the case of

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irreversible growth, for a time-independent flux and with neglect of desorption [3-5, 12, 14, 18-21]), is that their solutions feature the scaling behavior for sufficiently large clusters. There are several formulations of this scaling given, e.g., by Vicsek and Family [3] and then developed by Korner *et al.* [14], or those considered by Bartelt and Evans [4]. The most common formulation [4-7, 12-14, 16-21] states the following. For large enough size s, the SD over s at time t, $f_s(t)$, is expected to have the form $f_s(t) = [\Theta / < s >^2] \varphi(s / < s >)$, where $\Theta \propto t$ is the coverage, $< s >$ is the time-dependent mean size and φ is a certain universal, time-invariant function of the scaled cluster size $s / < s >$. If the asymptotic mean size equals the coverage in the appropriate normalization, i.e., $< s > \cong \Theta$, the general expression is reduced to $f_s(t) = [1 / < s >] \varphi(s / < s >)$. Obviously, such a scaling behavior is of great help for theoretical analyses and would determine the properties of the physical averages.

As discussed in Ref. [16], the scaling in terms of the scaled size $s / < s >$ would not pertain in physical SDs for all growth times and sizes s unless the ratio of the diffusion constant over the deposition rate is infinitely large [4] (which is the typical scenario in low-temperature surface growth). In the latter, regime, the scaling functions are often non-analytic [4, 12, 16]. This can be shown rigorously in the case of the mean field capture numbers which are proportional to s^p with $0 \le p < 1$. The refined scaling, working for a much wider range of conditions and much smaller s, should be searched for in terms of the variable $(s_*^{\alpha} - s^{\alpha}) / s_*^{\beta}$, with s_* being proportional to $< s >$ and α, β being the power indices which depend on p [16]. Of course, the mean field approach itself fails when subtle correlations between island size and separation affect the effective capture coefficients and thus control the SD shapes [5, 19].

In this paper, we study theoretically the case of heterogeneous nucleation with the size-linear rate constants for aggregation and fragmentation. Such a size-linear dependence has been previously considered, e.g., in the context of birth-death processes [28], however, usually without accounting for a time-dependent concentration of monomers. Under certain assumptions, size-linear model could be applied for several systems such as vertical nanowires collecting growth species from the sidewalls [26], two-dimensional clusters growing directly from vapor [23], some of the one-dimensional rows on a solid surface [7, 17] (if adatoms are captured on the sides of rows and then diffuse to the ends), and linear peptide chains in water solutions [15].

It will be shown that the size-linear heterogeneous model with fragmentation has two distinctly different regimes. The first regime corresponds to a stable growth, which could be either infinite or limited depending on the flux. In the second, unstable growth regime, smaller clusters would decay and larger grow, as in nucleation theory with a time-dependent critical size [26]. We then obtain analytical solutions of the corresponding mean field REs for the discrete SD, expressed through the Polya distribution. These solutions are exact in the stable case and only asymptotic in the unstable case (with termination of the flux). The solution in the stable case has the scaling form in terms of the $s / < s >$ variable for all but very small s, and does not require any additional assumptions such as infinitely high diffusivity or a time-independent influx. The particular case of the scaling function is exponential, and coincides with the one describing homogeneous irreversible growth with size-linear capture coefficients. Conversely, the scaling form of the asymptotic SD is lost in the unstable case. It is also lost in the stable growth regime when the aggregation rate constants become size-independent. We consider some experimental SDs for linear surface rows of metal atoms on Si(100) [7, 17] and demonstrate their reasonable fits with our exact solution in the stable heterogeneous case.

2. Rate equations of heterogeneous nucleation

We consider a heterogeneous growth process involving aggregation and fragmentation of clusters via the scheme $A_sB + A_1 \Leftrightarrow A_{s+1}B$ with $s = 0, 1, 2, 3...$ Here, B denotes the nucleation center (such as a charged ion in vapor or reactive defect on a solid surface), A_1 is the free monomer and A_sB is the cluster consisting of s monomers and one nucleation center. By definition, $A_0B \equiv B$ is the free seed. The set of REs for the concentrations of free monomers $n_A(t) = [A_1]_t$ and clusters $n_s(t) = [A_sB]_t$ (at $i = 0$, $n_0(t) = [B]_t$ is the concentration of free nucleation centers) is given by

$$\frac{dn_A}{dt} = -\sum_{s=1}^{\infty} J_i + R;$$

$$\frac{dn_s}{dt} = J_s(1-\delta_{so}) - J_{s+1},\ s \geq 0;$$

$$J_s = K_{s-1}^{+} n_A n_{s-1} - k_s^{-} n_s,\ \ s \geq 1. \qquad (1)$$

Here, K_s^{+} is the aggregation rate constant, k_s^{-} is the fragmentation rate constant, J_s is the flux along the size axis showing how many clusters are transferred from the state with the size $s-1$ to s per unit time, and $R = const$ is the external influx of monomers A_1. Kroneker's symbol δ_{so} disables the decay of nucleation centers B. The first equation shows that the concentration of free monomers changes whenever a monomer is attached to or detached from a cluster, and due to the material influx. According to the second equation, the concentration of clusters of a given size changes in time due to the difference between the two fluxes going into and from the state with the size s and becomes time-independent at equilibrium ($J_s = 0$) or in a steady state (i.e., when $J_s = J$ is size-independent). Clearly, the equilibrium state can be reached only in systems with fragmentation, while for irreversible growth $J_s = K_{s-1}^{+} n_A n_{s-1}$ can become zero only in a materially isolated system when $n_A \to 0$.

REs given by Eqs. (1) yield the following conservation laws:

$$\sum_{s=0}^{\infty} n_s(t) = n_B^{tot};\ \ n_A(t) + \sum_{s=1}^{\infty} s n_s(t) = n_A(0) + Rt\,. \qquad (2)$$

The first equation gives the conservation of total number of nucleation centers, and the second one shows that the total number of monomers increases with time only due to the external flux. As the major simplification within this heterogeneous growth model, the total number of all clusters plus the number of free nucleation centers equals the total number of nucleation centers $n_B^{tot} = const$ at any time. This feature is distinctly different from homogenous nucleation where the total number of clusters is not conserved [26]. It is therefore convenient to consider the normalized size distribution $f_s(t) = n_s(t)/n_B^{tot}$ for which $\sum_{s\geq 0} f_s(t) = 1$, and the normalized monomer concentration $f_A(t) = n_A(t)/n_B^{tot}$. The aggregation rate constants can be put in the form $K_i^{+} = k_i^{+} n_B^{tot}$, where k_i^{+} have the same dimension (of the inverse time) as k_i^{-}.

As in Ref. [31], we now assume that the rate constants of whatever origin depend linearly on the number of monomers in the cluster:

$$k_0^+ = k^+ b;\ k_s^+ = k^+(a-1+s),\ s \geq 1;\ k_s^- = k^- s,\ s \geq 1, \quad (3)$$

with some positive dimensionless parameters b, a and the constants $k^\pm$ having the dimensions of the inverse time. Of course, such a form can hardly be rigorously justified in concrete systems for any size and should be considered as an approximate model (also because simple mean-field treatments of rate constants often fails to describe size distributions in systems without desorption and at high diffusivity). However, it can be treated as the first terms in the Taylor expansion of arbitrary $k_s^\pm$ in s near $s = 0$, where k_0^- must be zero to disable the decay of nucleation centers. Realistically, linear aggregation rate constants k_s^+ would apply only for some model systems such as shown in Fig. 1: two-dimensional surface clusters growing directly from vapor, vertical nanowires fed from a vapor phase through their sidewalls, and surface nanowires in situations where adatoms are captured on their sides of rows and diffuse to the ends. If the capture just occurs at the ends of surface rows, as suggested, e.g., in Ref. [7], the aggregation rates become size-independent corresponding to the formal limit $a \to \infty$ in Eqs. (3), which will also be considered below.

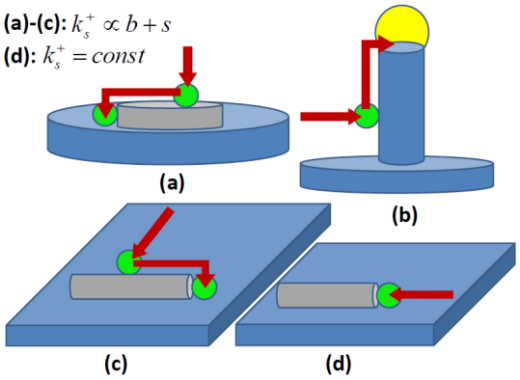

Fig. 1. Illustration of growth systems with linear size dependence of the aggregation rates $k_s^+ \propto b + s$: two-dimensional surface islands growing by direct impingement from vapor (a); one-dimensional vertical nanowires which collect growth species from its sidewalls (b), one-dimensional surface chains in situations where adatoms are captured on the sides of chains and then diffuse to the ends (c). Another possible scenario is the direct impingement of atoms from vapor onto the chain with subsequent migration to the ends. If capture just occurs at the ends, the growth rate becomes independent on the chain length: $k_s^+ = const$ (d).

With these linear rate constants and after the appropriate renormalization, the set of the REs given by Eqs. (1) for the SD $f_s(\tau)$, expressed in terms of the dimensionless time $\tau = k^- t$, writes down as

$$\frac{df_0}{d\tau} = -b(\zeta+1) f_0 + f_1;$$

$$\frac{df_1}{d\tau} = b(\zeta+1) f_0 - f_1 - a(\zeta+1) f_1 + 2 f_2;$$

$$\frac{df_s}{d\tau} = (a-2+s)(\zeta+1) f_{s-1} - s f_s - (a-1+s)(\zeta+1) f_s + (s+1) f_{s+1},\ s \geq 2. \quad (4)$$

Here, we introduce the new time-dependent variable, $\zeta \equiv (k^+/k^-) f_A - 1$, which has a clear sense of the effective supersaturation of a free monomer "vapor" with the concentration f_A.

This ζ depends on time and can have either signs. The mean size of clusters, $< s >= \sum_{s\geq 1}^{`} s f_s$, obeys the equation

$$\frac{d < s >}{d\tau} = \zeta < s > + (1-a)(\zeta+1)(q f_0 - 1), \quad q \equiv (b+1-a)/(1-a). \tag{5}$$

The material balance of monomers given by Eq. (2) can be put in the form

$$\Theta = < s > + (k^- / k^+)\zeta. \tag{6}$$

The appropriately normalized coverage, $\Theta = (k^- / k^+)\zeta(0) + (R\tau)/(n_B^{tot} k^-)$, equals the so-called "ideal supersaturation" in the absence of any clustering, i.e., when $< s >= 0$ [26]. The coverage increases linearly with time in open systems and is conserved in isolated systems with $R = 0$. In principle, Eqs. (5) and (6) allow for the determination of the mean size and supersaturation as functions of time. At the beginning of the growth process, the system does not contain any clusters, i.e. $f_0(\tau = 0) = 1$ and $f_s(\tau = 0) = 0$ for all $s \geq 1$, yielding also $< s > (\tau = 0) = 0$.

We note that the system considered is expected to have rather different behaviors depending on whether $a > 1$ or $a < 1$. Indeed, the growth rate of a cluster consisting of s monomers can be generally defined as $ds/dt = k_s^+ f_A - k_s^-$. With our size-linear rate constants given by Eqs. (3), this is reduced to $ds/d\tau = (a-1)(\zeta+1) + \zeta s$. At $a > 1$, the cluster growth rate is positive for all s at $\zeta > 0$. Hence, a positive supersaturation yields an unlimited growth of clusters regardless of their size. This is effectively the irreversible growth case studied in Refs. [4, 5, 12, 16]. When $\zeta < 0$, the growth rate becomes zero at a stable point such that smaller clusters would grow and larger clusters decay, corresponding to a limited stable growth. Whenever $a < 1$, a positive supersaturation leads to the growth instability such that smaller clusters decay and larger clusters grow, as in nucleation theory with a supersaturation-dependent critical size [22-26]. In our model, this critical size corresponds to the condition $ds/d\tau = 0$ and equals $i = (1-a)(\zeta+1)/\zeta$. When $\zeta < 0$, all the clusters would decay regardless of their size. Consequently, we will call the situation with $a > 1$ the stable growth (which can be either unlimited or limited depending on the monomer influx), while the case $a < 1$ will be referred to as the unstable growth. The mathematical difficulty in the unstable case arises from the fact that the parameter q in Eq. (5) cannot be put to zero and hence the mean size depends on the concentration of free nucleation centers f_0. The latter is generally unknown and requires a solution of the entire infinite set of the REs.

3. Analytical solutions

We start the analysis with the general case of arbitrary positive a and b. As in Refs. [4, 26, 27, 30, 31], we introduce the generating function for the discrete SD by definition

$$f(x,\tau) = \sum_{s=0}^{\infty} f_s(\tau) x^s, \tag{7}$$

having the obvious properties $f(0,\tau) = f_0(\tau)$ and $f(1,\tau) = 1$. Differentiating Eq. (7) with respect to time and using Eqs. (4), we obtain the first-order partial differential equation for $f(x,\tau)$:

$$\frac{\partial f}{\partial \tau} = (x-1)\left\{[(\zeta+1)x - 1]\frac{\partial f}{\partial x} - (1-a)(\zeta+1) f + (b+1-a)(\zeta+1) f_0\right\};$$

$$f(x,\tau=0)=1. \tag{8}$$

Obviously, $<s>=[\partial f(x,\tau)/\partial x]_{x=1}$, and hence Eq. (5) for the mean size actually follows from Eq. (8). For the new function $F(x,\tau)$ defined as

$$F(x,\tau)=f(x,t)-qf_0(\tau), \tag{9}$$

the equivalent equation has the form

$$\frac{\partial F}{\partial \tau}=(x-1)\left\{[(\zeta+1)x-1]\frac{\partial F}{\partial x}-(1-a)(\zeta+1)F\right\}-q\frac{df_0}{d\tau};$$

$$F(x,\tau=0)=1-q, \tag{10}$$

which is more convenient is what follows.

Exact solution to Eq. (10) is given by

$$F(x,\tau)=[1+\alpha(\tau)(1-x)]^{1-a}\left\{1-q-q\int_0^\tau d\tau'\left(1+\frac{e^{-z(\tau')}\alpha(\tau')}{\Psi_1}\right)^{1-a}\frac{df_0}{d\tau'}\right\}, \tag{11}$$

with the first integral $\Psi_1(x,\tau)$ in the form

$$\Psi_1(x,\tau)=e^{-z(\tau)}\left(\frac{1}{1-x}-\alpha(\tau)\right). \tag{12}$$

Here, the functions $z(\tau)$ and $\alpha(\tau)$ are defined as

$$z(\tau)=\int_0^\tau d\tau'\zeta(\tau'); \tag{13}$$

$$\alpha(\tau)=e^{z(\tau)}\int_0^\tau d\tau'[\zeta(\tau')+1]e^{-z(\tau')}. \tag{14}$$

Obviously, the function α obeys the equation

$$\frac{d\alpha}{d\tau}=\zeta\alpha+\zeta+1;\ \alpha(\tau=0)=0. \tag{15}$$

Now, the general procedure for obtaining the SDs is the following. We should first put $x=0$ in Eq. (11), which gives an integral equation for the unknown concentration of free nucleation centers $f_0(\tau)$. Solving it, we insert the result into the right hand side of Eq. (11) and obtain a closed equation for the generating function. Solving this equation and then expanding it in x would give the resultant SD. Unfortunately, analytical and even numerical implementation of this scheme is far from straightforward in the general case.

We now consider the asymptotic solution to Eq. (11) which corresponds to the approximation $1+e^{-z(\tau')}\alpha(\tau')/\Psi_1\cong 1$ under the integral. This reduces the integral to simply $1-qf_0(\tau)$. Apparently, such an approximation is equivalent to applying the Laplace method for calculating the integral in the right hand side of Eq. (11), which should be justified when $df_0/d\tau$ is a steep function near $\tau=0$. This should hold for $b>>1$ and hence $q>>1$. The

corresponding approximate solution has the form

$$F(x,\tau) \cong \left[1+\alpha(\tau)(1-x)\right]^{1-a}[1-qf_0(\tau)]. \tag{16}$$

Using the normalization condition, we arrive at the following SD

$$f_0(\tau) = \frac{[1+\alpha(\tau)]^{1-a}}{1+q[1+\alpha(\tau)]^{1-a}-q}; \qquad f_s(\tau) = \frac{<s>(\tau)}{s} f_{s-1}^{(a)}[\alpha(\tau)],\ s \geq 1. \tag{17}$$

Here,

$$<s>(\tau) = \frac{b\alpha(\tau)}{1+q[1+\alpha(\tau)]^{1-a}-q}, \tag{18}$$

is the mean size of the approximate SD. Here and below, we use the notation

$$f_s^{(c)}[\alpha] = \frac{\Gamma(c+s)}{\Gamma(c)s!}\frac{\alpha^s}{(1+\alpha)^{c+s}},\ s \geq 0 \tag{19}$$

for the Polya distribution with the mean size $<s>=c\alpha$, where $\Gamma(y)$ denotes the gamma-function.

This SD has the following important properties:

1) In the stable growth with $a>1$, we can put

$$b = a-1, \tag{20}$$

corresponding to $q=0$ and $k_s^+ = k^+(b+s)$ for all $s=0,1,2...$, i.e., a purely linear size dependence of the aggregation rate constants. In this case, Eqs. (17) are reduced to the exact solution which has the form of the Polya distribution with the parameter $b>0$ and the mean size $b\alpha$ [31]:

$$f_s(\tau) = f_s^{(b)}[\alpha] = \frac{\Gamma(b+s)}{\Gamma(b)s!}\frac{\alpha^s}{(1+\alpha)^{b+s}},\ s \geq 0,\ <s>=b\alpha. \tag{21}$$

This can be represented in terms of the mean size $<s>$ as

$$f_s^{(b)}[<s>] = \left(1+\frac{<s>}{b}\right)^{-b}\frac{\Gamma(b+s)}{\Gamma(b)s!}\left(\frac{<s>}{<s>+b}\right)^s. \tag{21a}$$

In the formal limit $b \to \infty$, for which the rate constants become size-independent, the Polya distribution is reduced to the Poissonian SD

$$f_s[<s>] = e^{-<s>}\frac{<s>^s}{s!}. \tag{22}$$

2) In the unstable case with $a<1$, it can be shown that the approximate solution given by Eqs. (17) matches exactly the equilibrium SD at $\tau \to \infty$ in a closed system ($\Theta = const$) or upon the flux termination ($\Theta \to \Theta_{max}$). Of course, the equilibrium solution exists only when the final supersaturation is negative ($\zeta \to \zeta_\infty < 0$).

3) By its form, Eq. (17) might seem to be a discrete analogue of the continuum Lifshitz-Slyozov transformation of variables if the mean size equals or is proportional to the critical size: $<s>=\xi i$ [32]. Indeed, regardless of the particular form of the normalized SD in the

right hand side, we always resume the property $\sum'_{s\geq 1} s(<s>/s) f_{s-1} = <s> \sum'_{s\geq o} f_s = <s>$. This transformation is the essential step in construction of the famous solution at the ripening stage in a closed system [32]. However, we will show later that the continuum form of the f_s in our solution in the unstable case is not a unique scaling function of the scaled size $s/<s>$ or s/i, as required in the Lifshitz-Slyozov theory of ripening.

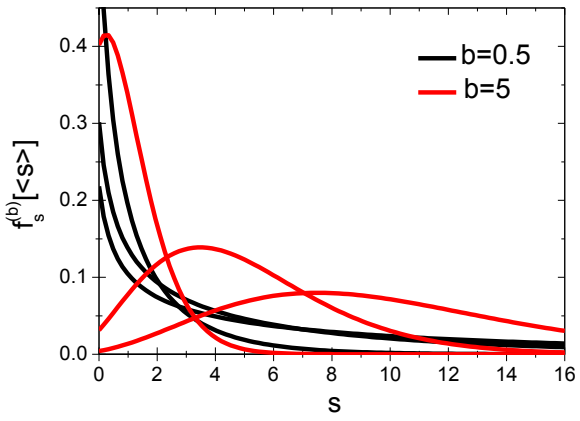

Fig. 2. Polya distributions at $b = 0.5$ and 5 for $<s>$=1,5 and 10.

The Polya distributions given by Eq. (21a) at b = 0.5 and 5 for three different $<s>$ are shown in Fig. 2. These SDs remain monotonically decreasing at $b \leq 1$ (the particular case of $b = 1$ gives the decreasing geometrical distribution), while at $b > 1$ they have a monomodal form with a maximum. Thus, the tendency to acquire a monomodal form of the SD is observed for larger b in the size-linear growth rate $k_s^+ = k^+(b+s)$. The limiting case of $b >> 1$ relates to the size-independent growth constants and the monomodal Poissonian SD. Of course, the same feature pertains for irreversible growth at $k^- = 0$. Furthermore, the analysis of the irreversible homogeneous growth with $k_s^+ = k^+(b+s-1)$ (Ref. [26]) also reveals a decreasing SDs at small b, while monomodal SDs are observed for large b.

This conclusion might seem counterintuitive at first glance. Indeed, it seems that higher growth rates of large clusters should boost their population with respect to smaller ones. However, this is not the case for the following reason. The aggregation constant at $s = 0$, $k_0^+ = k^+ b$, gives the probability of nucleation of the very first heterogeneous particle in the reaction $A_1 + B \rightarrow A_1 B$, while $k_s^+ \cong k^+ s$ at $s >> b$ describes the aggregation of large clusters. Small b values relate to situations where the initial nucleation of the $A_1 B$ "dimers" is suppressed, i.e., aggregation is preferred to the formation of dimers. In this case, the limiting stage of the entire growth process is nucleation. Consequently, the concentration of the free nucleation centers (which cannot be filled due to a suppressed nucleation) will remain the most representative in the distribution, leading to the monotonically decreasing SD as in Fig. 3 at $b = 0.5$. In the opposite case of large b, nucleation of dimers is preferred to aggregation. This rapidly decreases the population of the free nucleation centers. The newly formed small clusters rapidly grow and the SD maximum propagates to the right, yielding the monomodal shape which is shown in Fig. 2 at $b = 5$.

4. Large time asymptotes under material influx

In the stable case ($a > 1$) under a time-independent material influx, the coverage increases linearly with time in the large time limit:

$$\Theta = \frac{\tau}{\tau_0}, \tag{23}$$

where τ_0 is the macroscopic time related to the influx R in Eq. (1) (e.g., vapor flux for surface clusters) as $1/\tau_0 = R/(k^- n_B^{tot})$. From the material balance given by Eq. (6) and assuming $\zeta \to 0$, we get: $< s > \cong \Theta = \tau / \tau_0$, i.e., the mean size asymptotically equals the coverage and increases linearly with time due to the monomer influx. Using this in Eq. (5) at $q = 0$, $b = a - 1 > 0$ and $\zeta \to 0$, and then in Eq. (15), we obtain

$$\zeta \cong \frac{1 - b\tau_0}{\tau}; \ \alpha = \frac{< s >}{b} \cong \frac{\tau}{b\tau_0}. \tag{24}$$

Therefore, supersaturation scales with time as $1/\tau$ and remains infinitely small positive when $b\tau_0 < 1$, while α increases linearly with time along with the mean size.

It is noteworthy that the approximate solution given by Eqs. (17) in the unstable case cannot hold if the material influx remains on at $\tau \to \infty$. Indeed, at $\Theta \to \infty$ we should also observe $\alpha \to \infty$. From Eq. (18) at $\alpha >> 1$ it then follows that

$$< s > \cong \frac{b}{q} \alpha^a, \tag{25}$$

showing that the mean size increases slower than α. Further, from Eq. (17) for f_0 at $\alpha >> 1$ we get

$$f_0 \cong \frac{1}{q} \left\lfloor 1 + \frac{(q-1)}{q} \alpha^{a-1} \right\rfloor. \tag{26}$$

For the non-trivial $(1-a)(\zeta+1)(qf_0 - 1)$ term in Eq. (5) for the mean size, this yields $(1-a)(\zeta+1)(qf_0 - 1) \cong (b/q)(\zeta+1)\alpha$. Using this and substituting Eq. (25) into Eq. (5), we arrive at

$$a \frac{d\alpha}{d\tau} = \zeta\alpha + \zeta + 1. \tag{27}$$

Obviously, this is consistent with Eq. (15) only when $d\alpha / d\tau \to 0$, so both α and $< s >$ must saturate at $\tau \to \infty$, which necessarily requires $\zeta \to \zeta_\infty < 0$. Asymptotic properties of the unstable system with a continuous influx require a separate study which will be presented elsewhere.

5. Continuum size distributions and scaling

Using the Stirling formula and the asymptote $\left(\alpha/(1+\alpha)\right)^s = \exp(-s/\alpha)$ for large s and α, we arrive at the continuum form of the Polya distribution at $s >> 1$

$$f^{(c)}(s,\alpha) = \frac{s^{c-1}}{\Gamma(c)\alpha^c} \exp(-s/\alpha). \tag{28}$$

This continuum SD obeys the normalization condition and preserves the correct mean size:

$$\int_0^\infty ds f^{(c)}(s,\alpha) = 1; \qquad \int_0^\infty ds s f^{(c)}(s,\alpha) = c\alpha. \tag{29}$$

It is easy to see that Eq. (28) has the scaling form

$$f^{(c)}(s,\alpha)=\frac{1}{\Gamma(c)\alpha}\left(s/\alpha\right)^{c-1}\exp(-s/\alpha)\,. \tag{30}$$

Therefore, in the stable case $a>1$, $b=a-1>0$, the continuum SD obeys exactly the scaling law in terms of the scaled size $s/<s>$

$$f^{(b)}(s,<s>)=\frac{1}{<s>}\varphi_b\left(\frac{s}{<s>}\right)=\frac{\Theta}{<s>^2}\varphi_b\left(\frac{s}{<s>}\right), \tag{31}$$

with the $b-$dependent scaling function given by

$$\varphi_b(x)=\frac{b^b}{\Gamma(b)}x^{b-1}e^{-bx}\,. \tag{32}$$

The second equality in Eq. (31) holds because $<s>=\Theta$ at small enough ζ.

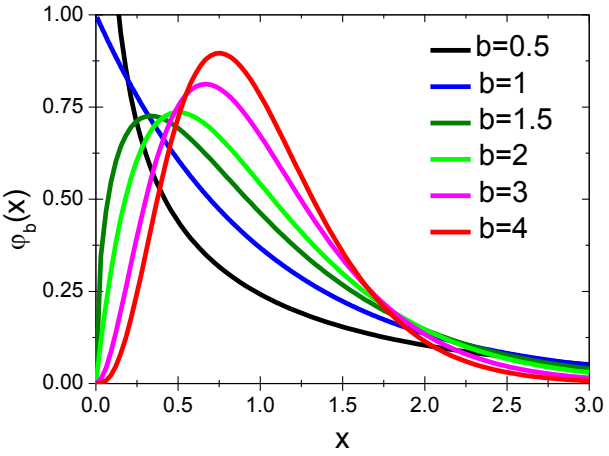

Fig. 3. Scaling functions $\varphi_b(x)$ for different b.

Very importantly, the scaling given by Eqs. (31) and (32) is the intrinsic property of the heterogeneous growth model with the size-linear rate constants and does not require any other assumptions. Indeed, in deriving these equations, we have not assumed that the surface diffusion constant is large compared to the flux and even that the flux is always on. Equations (31) and (32) pertain for systems with decay of clusters, isolated systems and also when desorption is included. This scaling can therefore be applied to almost all islands starting immediately from the moment of time when they are seen in the SD. It is clear that $\varphi_b(x)$ is singular at $x=0$ for $b<1$ and monotonically decreases for $b\le 1$. At $b>1$, the $\varphi_b(x)$ has a maximum which is shifted toward larger x for larger b, as shown in Fig. 3.

If the aggregation rate constant is size-independent ($b\to\infty$), the corresponding Poissonian SD is given by Eq. (22). This is the only stable case where the scaling in terms of the scaled $s/<s>$ variable does not hold because the Poissonian SD rapidly tends to the Gaussian

$$f(s,<s>)=\frac{1}{\sqrt{2\pi<s>}}\exp\left[-\frac{(s-<s>)^2}{2<s>}\right]. \tag{33}$$

Such a SD cannot be presented as a time-invariant analytic function of the scaled size

$s/<s>$, as discussed in Ref. [16], while the formal limit at $<s>\to\infty$ yields the non-analytic Bartelt-Evans scaling [4] for both small and large sizes.

In the unstable case with $a<1$, in situations described by the approximate solutions given by Eqs. (15) (we already know that these expressions apply near equilibrium for isolated systems and do not apply under the monomer influx), we can still use Eq. (26) at $s>>1$ and $\alpha>>1$. Using Eq. (26) at $c=a$ in Eq. (15) and then Eq. (23), we obtain

$$f(s,<s>)=\frac{1}{<s>^{2-a}}\frac{p}{\Gamma(a)}\left(\frac{s}{<s>}\right)^{a-2}\exp\left(-p^{1/a}\frac{s}{<s>^{1/a}}\right), \tag{34}$$

with $p=b/q$. It is seen that this function does not have a scaling form in terms of the scaled cluster size $s/<s>$. Indeed, the scaled SD is given by

$$f(s,<s>)<s>=\frac{p}{\Gamma(a)}\frac{1}{<s>^{1-a}}x^{a-2}\exp\left(-\frac{p^{1/a}}{<s>^{1/a-1}}x\right), \tag{34a}$$

which is not a unique function of $x=s/<s>$ and tends to a singularity at $x=0$ when $<s>\to\infty$ (see Fig. 4). The absence of scaling is explained by the non-linear relation between $<s>$ and α given by Eq. (23). As for the Lifshitz-Slyozov theory of ripening [32], it requires that ζ at the asymptotic stage is small positive. In the linear model, this occurs only in systems with continuous influx where our approximate solution is not valid, as discussed above. In a closed system, supersaturation tends to a negative value and thus the ripening process is disabled.

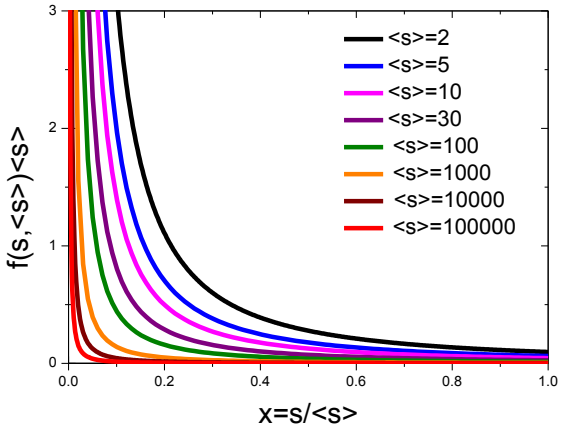

Fig. 4. Evolution of the scaled SD $f(s,<s>)<s>$ in the case $a=b=1/2$ showing the absence of scaling in the unstable case with $a<1$.

6. Fitting experimental size distributions

Let us now see how the obtained analytical solutions can be used for fitting the experimental data on different one-dimensional surface chains. For surface islands, assuming a heterogeneous character of nucleation, the growth rate constants would have the form $k_s^+=n_{tot}D\sigma_s$, where n_{tot} is the surface concentration of the nucleation centers (e.g., surface steps [33] or defects [17]), D is the diffusion coefficient of a mobile adatom, and σ_s is the size-dependent capture number. Linear surface rows are formed rather than islands if the disusing adatoms can bond with rows only at the two end sites [7].

In Ref. [7], room temperature deposition of Ga onto Si(100) with a deposition rate 10^{-3} monolayers (MLs) per second produced single-atom-wide Ga rows which lie orthogonal to

the Si-dimer rows on the clean 2×1 reconstructed Si(100) surface. Scanning tunneling microscopy (STM) measurements of the length distributions at different metal coverages revealed the decreasing SDs for these rows, as shown in Fig. 5 (a) (although a "weak" peak for small sizes was not excluded). Figure 5 (b) shows the same SDs in scaling variables $f(s)<s>$ and $s/<s>$. As discussed in Ref. [7], this decreasing behavior is unusual since most theoretical models predict a monomodal shape with well-defined peak of the scaled SDs around $x=1$ for both homogeneous [4, 5, 12] and heterogeneous [34, 35] nucleation. Monomodal SD shapes were also observed experimentally for one-dimensional metal islands on anisotropic fcc(110) surfaces [36] and in Si(100) homoepitaxy at low temperatures [37]. Kinetic Monte Carlo simulations of atomistic models for homogeneous growth [7] explained the observed decreasing SDs by the unusually enhanced nucleation relative to aggregation.

Lines in Figs. 5 show the best fits of the experimental SDs of Ref. [7] by our model Eq. (21a) for the initial discrete SD and Eqs. (31), (32) for the continuum scaled SD. Since the experimental mean size $<s>$ is known for each sample, the only fitting parameter is the dimerization rate b, which appears to be of the order of one in all cases. It is seen that our simple expressions fit very well the data. We note that the model considered here is heterogeneous and assumes nucleation on foreign centers, such as C-type defects on Si(100)-2×1 [17], reported to be very reactive and act as nucleation centers [38, 39]. Therefore, the interpretation of the decreasing SDs in our heterogeneous model is different from the original work [7], and suggests that the Ga rows are formed on surface defects, while their growth rate is roughly proportional to the length. As discussed above, this could occur if the diffusing metal adatoms are captured along the entire length of the row but cannot be incorporated from the sides, and then migrate along the chain and finally incorporate to the edges. It should be pointed out that the authors of Ref. [7] themselves discuss a possibility for forming a decreasing SD by nucleation mediated by irreversible exchange of single adatoms with the substrate, a heterogeneous process sometimes described as having a critical size $i_c=0$ [40].

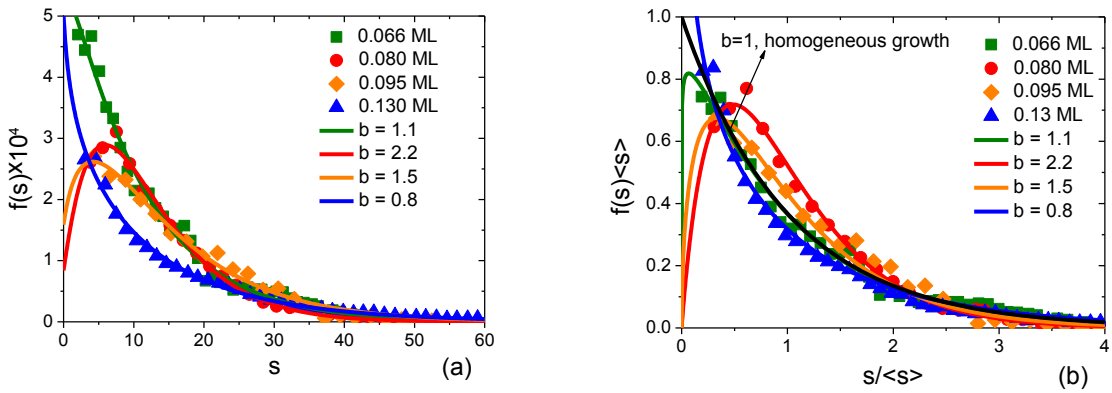

Fig. 5. Size distributions of single-atom-wide Ga rows on Si(100) at different metal coverages (symbols) [7] and their best fits by Eq. (21a) for a given mean size and at different b (colored lines) (a); panel (b) shows same distributions in scaling variables, fitted by Eqs. (31) and (32). The black line in (b) shows the exponential fit at $b=1$, which is also the result of homogeneous growth model with size-linear rate constants.

Figure 6 shows the scaled SDs for one-dimensional In adatom chains deposited onto Si(100)-2×1 surface [17] at 0.04 and 0.08 ML coverage [17]. These chains were obtained by In deposition at room temperature and characterized by STM. In this work, the island growth process was deemed to proceed via a heterogeneous process, since the In chains were shown to terminate at C defects, while the initial concentration of C defects was unchanged. The

curves demonstrate that the scaled SDs for both In coverages are purely decreasing, with a very high population near $x=1$. The best fit by Eqs. (31) and (32) is obtained, however, at $b=2.3$, and has a maximum at $x\cong 0.6$, and thus we are unable to describe correctly the two maximum points at thee 0.08 ML coverage. The discrepancy between the theoretical fit and the data might be due the postdeposition relaxation, as discussed by the authors [17]. Overall, the fits shown in Figs. 5 and 6 are quite reasonable, however, they require the assumption on the heterogeneous character of nucleation.

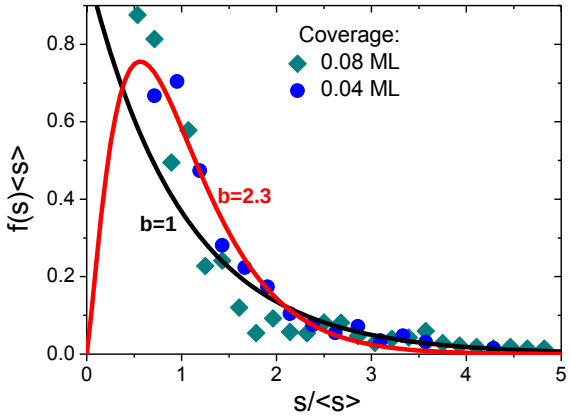

Fig. 6. Scaled size distributions of In chains on Si(100)-2×1 at two different coverages [17], and their best fit by Eqs. (31) and (32) at $b=2.3$ (red line). The black line at $b=1$ corresponds to the exponential fit.

The role of heterogeneous versus homogeneous nucleation of metal surface rows on Si surfaces such as described in Refs. [7, 17, 39] remains an open question. In particular, Albao *et al*. [41] argued and presented some evidence that growth of Ga chains on Si(100) is not dominated by heterogeneous nucleation at C defects, contrasting the proposal of Kocán *et al*. [39] and the assumption of Ref. [17]. Probability of heterogeneous nucleation should depend on concentration of the reactive defects. As demonstrated theoretically in Ref. [42], concentration of the defects larger than 0.0025 per site may change the island SDs from monomodal to monotonically decreasing in the case of the irreversible growth model. Fragmentation of islands in systems close to equilibrium has been also found important for the SD shapes [42-44]. For example, the results of Ref. [43] suggest that the scaling functions are monotonously decreasing in quasi-equilibrium case with fragmentation, while in the case of irreversible growth they exhibit a monomodal character.

A comparison of heterogeneous versus homogeneous irreversible growths with size-linear capture coefficients will be presented elsewhere. We note, however, that the homogeneous irreversible growth model with size-linear capture coefficients $k_s^+ = k^+(1+s)$ for all s yields scaling in the form of Eq. (31) with the scaling function $\varphi_1(x)=\exp(-x)$, which is a particular case of Eq. (32) at $b=1$. Thus, the scaling functions of homogeneous and heterogeneous SDs at $b=1$ are exactly identical (which is of course not the case for arbitrary b). These exponential fits are shown in Figs. 5 (b) and 6 for comparison with the scaled heterogeneous SDs at $b\neq 1$. It is seen that the homogeneous exponential scaling function also provides a good fit to the scaled experimental SDs, especially in the case of Ga rows (Fig. 5 (b)). This is not surprising, because the fitting values of b are close to one.

7. Conclusion

In conclusion, we have presented the exactly solvable case of the stable heterogeneous nucleation including decay of clusters, with size-linear rate constants for aggregation and

fragmentation. The obtained SDs are given by the Polya distribution whose shape is controlled by the dimensionless dimerization constant b. Despite its simplicity, this SD has a rather general form and is capable of describing a monotonically decreasing SDs at $b \le 1$ and monomodal SDs with well-defined peak at $b > 1$. Similar distribution shapes apply for irreversible growth with no decay, in both isolated or open systems, and also when desorption is included (this would only change the kinetics of the mean size). Very importantly, the continuum form of the Polya SD automatically leads to scaling in terms of the $s/<s>$ variable. The model SDs have been shown to fit fairly well some experimental data for linear surface rows of metal adatoms on Si(100). The particular case of heterogeneous scaling function at $b = 1$ is exponential, and is identical to the case of homogeneous irreversible growth.

In the unstable model with a time-dependent critical size, we have obtained the asymptotic solution which applies near the equilibrium state in a closed system or upon termination of the influx. This solution does not yield a scaling form of the SD, because the mean size increases more slowly due to enhanced fragmentation of clusters. However, our approximate SD does not work for systems with a continuous influx, for example, in the case of surface islands deposited from a time-independent flux. Here, non-trivial effects such as breaking the SD into stable and irreversibly growing branches near the critical size and the asymptotic ripening stage are anticipated [32, 45, 46], which remain to be studied.

Acknowledgement

V.G. Dubrovskii acknowledges the financial support by the Russian Science Foundation under the Grant No. 14-22-00018. Yu.S. Berdnikov thanks the support by FP7 projects NANOEMBRACE (Grant Agreement 316751).

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