# Size distributions of fullerene surface clusters

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## ARTICLE INFO

## ABSTRACT

We present an exactly solvable generalization of the rate equation model for irreversible growth with size-independent capture numbers which includes desorption of monomers. It is shown that the universal size distribution shapes depend on the sole parameter, the ratio between the characteristic diffusion and adsorption areas. We perform a statistical analysis of the scanning tunneling microscopy images of $C_{60}$ clusters deposited onto In-modified Si(1 1 1)$\sqrt{3} \times \sqrt{3}$-Au surfaces at different temperatures and deduce the experimental size distributions. These distributions have an essentially asymmetric shape with a much faster decay toward larger sizes. Fitting the data with theoretical distribution shapes yield the estimates for some important kinetic parameters, in particular, the temperature-dependent diffusion lengths and effective lifetimes of $C_{60}$ monomers.

## 1. Introduction

Studies of size distributions of different "clusters" such as three-dimensional droplets [1], two-dimensional (2D) or three-dimensional surface islands [2–16] and one-dimensional nanowires [17] or linear peptide chains [18] is paramount for understanding their growth behavior as well as the resulting physical properties of the cluster ensembles. Theoretical approaches based on classical nucleation theory [1,4,5,19] apply whenever the clusters of interest consist of at least several tens of monomers and are terminated by distinct boundaries with a metastable phase. Such systems can be well described within the frame of classical approach involving macroscopic approximations for the formation energy and a continuum kinetic equation for time-dependent distribution of nuclei over sizes, coupled with the material balance.

In many cases, however, we deal with particles consisting of only a few monomers, while the decay of clusters can be neglected on a time scale of interest. In this case, the cluster formation is described within the mean field approach with discrete rate equations for irreversible growth [2,3,6–16,20,21], accounting for the influx and sink of monomers as well as for their consumption by growing clusters. For surface islands, the material influx is due to vapor deposition, while the sink originates from desorption from a substrate surface [15]. Irreversible growth models are much simpler for the analysis and may be even solved exactly for some particular forms of the capture numbers. On the other hand, continuum approximation is irrelevant for small clusters. Also, the mean treatment fails when subtle correlations between island size and separation affect the effective capture numbers and thus control the size distribution shapes. Comprehensive reviews of the advances in the theory of submonolayer surface growth, covering the mean field rate equations as well as a more complex approaches for the island size distribution can be found, e.g., in Refs. [9,21].

Here, we present an exactly solvable generalization of the discrete irreversible growth model for 2D islands with size-independent capture numbers (such a model was considered earlier, e.g., by Bartelt and Evans [7]), with desorption included. We show that the distribution shapes are determined by the sole dimensionless parameter, a combination of the deposition rate, the lifetime before desorption and the effective diffusion length of monomers. A more general theoretical analysis in the case of scaling size dependences of the capture numbers in systems with desorption, along with a discussion of the asymptotic scaling properties [7,9,21] is given in Ref. [20].

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Experimental part of the work deals with $C_{60}$ fullerene clusters deposited onto In-modified Si(1 1 1)$\sqrt{3} \times \sqrt{3}$-Au surfaces at different temperatures and then characterized by scanning tunneling microscopy (STM) [22–25]. Statistical analysis of STM images enables a precise determination of not only the temperature-dependent average size and density of clusters, but also of the size distributions. We find that the density of $C_{60}$ clusters decreases and their average size increases as the surface temperature increases, while the size distributions have an essentially asymmetric shape. We then fit the experimental size spectra with our model solutions and show a reasonable correlation of the results in all the cases considered. These fits allow us to estimate some important kinetic parameters of $C_{60}$ monomers such as diffusion lengths, effective lifetimes and activation energies.

## 2. Theoretical model of irreversible growth

In modeling of time-dependent concentrations $n_s(t)$ of the immobile surface clusters $A_s$ consisting of $s$ monomers (size $s$ for brevity), we assume that the clusters are fed by surface diffusion of the mobile monomers $A_1$ that have the diffusion coefficient $D$, arrive onto the surface at the time-independent rate $F$ and desorb from the surface with the characteristic time $t_{des}$. We neglect the decay of clusters on the time scale of interest, in which case the number of monomers in the critical cluster equals one and the cluster growth proceeds irreversibly: $A_s + A_1 \rightarrow A_{s+1}$, with $i = 1, 2, 3. \ldots$. The rate equations describing such an irreversible growth write down as [2,3,6–16,18,20,21]

$$\frac{dn_1}{dt} = F - \frac{n_1}{t_{des}} - 2D\sigma_1 n_1^2 - Dn_1 \sum_{s=2}^{\infty} \sigma_s n_s; \quad (1)$$

$$\frac{dn_s}{dt} = Dn_1(\sigma_{s-1}n_{s-1} - \sigma_s n_s) \quad s \geq 2, \quad (2)$$

with $\sigma_s$ as the corresponding capture numbers. Eq. (1) shows that the concentration of free monomers on the substrate surface changes due to their adsorption, desorption and consumption by the growing clusters, where the dimer formation requires two monomers. The chain of Eq. (2) shows that the concentration $n_s$ for each $s \geq 2$ increases when monomers attach to $s-1$-mers and decreases when monomers attach to $s$-mers. Summing up Eq. (2) for all $s \geq 2$, the surface density of clusters, $N = \sum_{s=2}^{\infty} n_s$, obeys the equation

$$\frac{dN}{dt} = D\sigma_1 n_1^2, \quad (3)$$

which gives the nucleation rate in irreversible growth. These rate equations should be solved with boundary conditions $n_s(t=0) = 0$ for all $s \geq 1$, i.e., neither monomers nor clusters are present at the beginning of deposition.

In our further analysis, we assume that $\sigma_s = \sigma_* = const$ for all $s \geq 2$ in the first approximation, so that each monomer is attached to a cluster with the size-independent sticking probability $\sigma_*$ when they meet. However, the capture number for adatoms $\sigma_1$ can be different from $\sigma_*$. In this case, Eqs. (1)–(3) are considerably simplified and can be put in the dimensionless form by introducing the dimensionless time $\tau = t/t_{des}$, the effective monomer diffusion length $\lambda = \sqrt{\sigma_* D t_{des}}$ (accounting for the capture number $\sigma_*$), the normalized cluster concentrations $f_s = \lambda^2 n_s$, the surface density $G = \lambda^2 N$, and the new time-dependent variable $z$ by definition

$$\frac{dz}{d\tau} = f_1, \quad z(\tau = 0) = 0. \quad (4)$$

Since all the growth rates now equal $f_1$ and are $s$-independent, the physical meaning of the $z$ variable is very simple [20]: it corresponds to the right boundary of the size distribution (i.e., to the
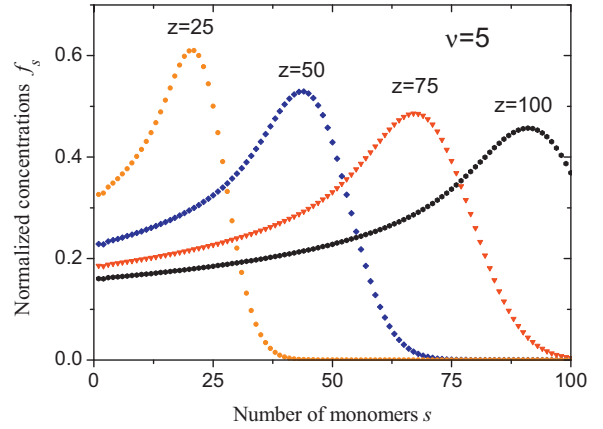


**Fig. 1.** Normalized concentrations $f_s$ at the fixed growth conditions ($\nu = 1$) and different $z$ relating to different growth times.

maximum possible size of clusters having emerged at $\tau = 0$) in the deterministic limit, where the SD shape is not affected by kinetic fluctuations [19].

In these variables, Eq. (1) for the monomer concentration and Eq. (3) for the island density become

$$\frac{df_1}{d\tau} = \nu - f_1 - 2bf_1^2 - f_1 G; \quad (5)$$

$$\frac{dG}{d\tau} = bf_1^2, \quad (6)$$

with $f_1(\tau = 0) = G(\tau = 0) = 0$. Here, the coefficient $b = \sigma_1/\sigma_*$ accounts for different capture number for adatoms and clusters. The control parameter $\nu$ is defined as follows:

$$\nu = \lambda^2 F t_{des} = \sigma_* D F t_{des}^2, \quad (7)$$

and has clear meaning of the number of monomers arriving from the vapor flux $F$ onto the surface area $\lambda^2 = \sigma_* D t_{des}$ during the time interval $t_{des}$.

Eq. (2) for the cluster concentrations become linear in terms of the $z$ variable:

$$\frac{df_2}{dz} = bf_1 - f_2$$
$$\frac{df_s}{dz} = f_{s-1} - f_s, \quad s \geq 3. \quad (8)$$

The exact solutions to this system are easily obtained by introducing the generating function for concentrations, as in Ref. [7]:

$$f_{s+2}(z) = \frac{b}{s!} \int_0^z dx f_1(z - x) x^s e^{-x}, \quad s \geq 0. \quad (9)$$

Here, the normalized concentration of free monomers $f_1$ is obtained as a function of $\tau$ from Eqs. (5) and (6) and then inverted as a function of $z$ by means of Eq. (4). This solution generalizes the earlier result of Bartelt and Evans [7] to systems with desorption, and is presented in terms of the $z$ variable which is more convenient for further analysis.

The discrete size distributions of differently sized clusters, computed from Eqs. (4) and (9), are shown in Figs. 1 and 2, for different deposition times ($z$) and deposition conditions ($\nu$), respectively. Here and below, we put $b = 1$ in calculations, however, reasonable variation of $b$ does not strongly affect the spectrum shapes. It is seen that the size distributions always have essentially asymmetric shapes, with an abrupt right tail and a much slower regression toward smaller $i$. It is noteworthy that these distributions are universal and depend on the sole parameter $\nu$, while fitting a particular