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Computational study on tuning the 2D self assembly of metallic nanoclusters

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ABSTRACT

We discuss the size selection of metallic 2D clusters in cases where the growth proceeds on flat or wedged surfaces. The growth of nanoclusters is modelled using reaction kinetic model rate equations, where the kinetics are described by size dependent attachment and detachment rates, and the energetics are described through the free energy difference of the clusters. The model describes how the optimum stationary size and small size dispersion are reached, and what are the properties of the stationary size distribution. In addition to the geometrical factors, it is shown that the deposition flux can also be used to tune the size distribution towards the desired property.

1. Introduction

Metallic nanoclusters are of much interest because of their unique properties and diverse technological applications [1,2]. The possibility to affect the self assembly process in a controlled and reproducible way would allow the fabrication of novel nanomaterials such as highly efficient quantum dots. Manufacturing quantum dot layers for optical or electronic devices requires, above all, narrow size distribution of clusters [3]. In other cases, optimal size dispersion of cluster sizes might be required. In addition, the possibility to tailor the specific voltage and optical wavelength of the material by shifting the size distribution of clusters in a controlled fashion would be very beneficial indeed. We investigate the possibility to tailor the expectation value, standard deviation and dispersion of cluster size distributions in a controlled way by varying two parameters essential to the growth process: the substrate geometry and the deposition flux of adatoms. Our first step is to evaluate the special case of how the growth proceeds on flat and wedged surfaces.

The effect of substrate geometry is particularly important when the nanocluster growth proceeds inside a supporting material e.g. a biopolymer matrix. Experimental studies on the final (stationary) state of Cu, Ni and Co nanoclusters, made inside a microcrystalline cellulose matrix, have shown that the nanocluster formation seems to be occurring at the pores and crevices on the cellulose fibres [4–6]. Unfortunately, the experimental examination of the actual process of nanocluster nucleation and growth *in situ* has received far less attention, mostly due to the fact that the available experimental probes have limited spatial resolution, or on the other hand, limited temporal resolution. At the advent of novel X-ray based probes using either modern synchrotrons or X-ray free electron lasers (XFEL), the spatial and temporal resolution for nanocluster growth studies is practically in our reach. Therefore the modelling of nucleation and growth theoretically and computationally have never been more topical.

The theoretical studies on nanocluster growth have mostly focused on semiconductor materials, especially in the cases involving self assembly, self organization and size selection [7–9]. The size uniformity of metal clusters is far less common, although some examples have been reported along with theoretical studies explaining the physical origin of such size selection [10–12]. The theoretical explanation of size selection in metallic nanoclusters is only the first, although very important, step in understanding the topic. A satisfactory explanation must include energetic as well as kinetic considerations, and the interplay between kinetics and energetics of growth makes analytical predictions in most cases impossible. The complexity of the problem requires a computational approach, and the traditional solving methods include Molecular Dynamics (MD) and Kinetic Monte Carlo (KMC) simulations. Although these methods have been used with much success, there are some troublesome limitations: the time scales and ensemble sizes required are well beyond the capabilities of MD, and KMC is still an unfeasible method for obtaining size distributions with good statistics. Therefore there is a considerable interest to model size selection in the mesoscopic level.

Thus, we describe the size selected growth of nanoclusters by using reaction kinetic model (RKM) rate equations, where kinetics are described by size dependent attachment and detachment rates, and energetics are described through the free energy difference of the clusters. The basic reaction kinetic equations and their justification have been discussed in detail in our previous publications [13,14] and are not reiterated here further. Here we concentrate on the question, how it becomes possible to tune the size distribution and find the optimum size distribution where the variance of sizes is at minimum

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i.e where size selection takes place with best perfection. This will not happen at spontaneously selected metastable state, instead the optimum size selection is expected only when finite flux is used to drive the distribution in larger sizes with smaller variance of sizes [15,16]. However, finding the optimum condition is computationally demanding and simplified models are needed to approach the problem. In effect, the present model describes how the optimum stationary size and small size dispersion are reached, and what are the properties of the stationary size distribution.

2. Theory

The basic physical assumptions behind the reaction kinetic model (RKM) are steady diffusion, total mass conservation and that the growing clusters are isolated dots in a dilute system. The model, the rate equations governing the growth, and the numerical calculations are discussed in detail in our previous studies [13,14] and references therein. In brief, the cluster growth is described through adatom attachment and detachment processes $A_1+A_s \leftrightarrow A_{1+s}$ with clusters of size s. The reaction rates for attachment and detachment are σ_s and γ_s, which are defined in terms of effective energy barriers Δ_s. The reaction rates used in this study are based on the self-consistent rate theory of Bales and Zangwill [17], with simplifying modifications which preserve the basic physical behaviour (for details, see the Appendix of Ref. [13]).

The kinetics of growth are taken into account in the reaction rates with a geometric size dependence s^q, i.e. the kinetics are simply related to the length of cluster boundary. The parameter q is thus related to the morphology of the growing clusters. Here we are mostly concerned with 2D compact clusters, thus $q=1/2$ is an appropriate choice.

The energetics of the model are defined through the total free energy E_s of the cluster of size s. The cluster growth is governed by cluster surface energy and cluster edge energy [10,11,18]. The total free energy is a sum of these contributions. The relevant quantity here is the free energy difference $\Delta_s = E_{s+1} - E_s$, which is proportional to the chemical potential of the clusters. The details are based on the model of dilute non-strained metal islands introduced by Feng Liu [11], and when adapted to our problem leads to the free energy difference with the form

$$\Delta_s(x) = -x^{-1}\log(ex) + 2\alpha e^{-\frac{1}{2}}x^{-\frac{1}{2}}, \tag{1}$$

where x is scaled size of the cluster s/s_0 and s_0 is the cluster size at the energy minimum. In brief, the first term corresponds to cluster surface edge energy and the second term corresponds to the surface energy of the clusters. Parameter α is a measure of strength of the edge energy to the surface energy and is of the order of unity. In addition, α is proportional to the geometry of substrate surface through a geometric factor which can be related to the opening angle of the wedge and to the cluster to substrate contact angle [11,19]. Roughly, the decrease of α to negative values corresponds to sharper wedge opening angles. On the other hand, the increase of α to positive values can be though as an upwards opening wedge i.e. the growth proceeds on top of a triangular surface. In this study, however, the values of the α-parameter are not directly related to any real system, mainly because it would require knowledge about specific parameters such as the surface energies of clusters and substrate, island-substrate interface energies and contact angles. Hence the chemical potential of Eq. (1) can be thought of as a generic result valid for large class of systems, and comparison with real systems would require additional knowledge of e.g. size minimum s_0 and depth of the chemical potential, which also are generally not known.

The time evolution of cluster size distribution in the RKM is calculated using rate equations for the adatom density n_1 and cluster densities n_s

$$\frac{dn_1}{dt} = \phi - 2\sigma_1 n_1^2 - n_1 \sum_{s\geq 2} \sigma_s n_s + \kappa\gamma_2 n_2 + \sum_{s\geq 2} \kappa\gamma_s n_s; \tag{2}$$

$$\frac{dn_s}{dt} = \sigma_{s-1} n_{s-1} n_1 - \sigma_s n_s n_1 + \kappa\gamma_{s+1} n_{s+1} - \kappa\gamma_s n_s, \tag{3}$$

where t is time, ϕ is the deposition flux of adatoms in monolayers (ML) per second and parameter κ defines the ratio of total detachment rate to the total attachment rate. These rate equations are based on the standard kinetic equation in nucleation theory, also known as Becker–Döring equations [20]. Similar equations have been used widely in various nucleation and growth problems (for details see e.g. the work of Zinsmeister [21] and the review by Kashchiev [22]).

The RKM rate equations, although perfectly valid for growth under finite flux, are extremely difficult to solve for size distributions. In addition, the numerical solution methods are bottlenecked by the term governing the time evolution of adatom density. The bottleneck is bypassed here with simplifications to the rate equations: the adatom density is assumed stationary in time, and the direct merging of two adatoms to form dimers is prevented. These assumptions lead to an approximate form of the rate equations

$$\frac{dN_1}{dt} = 0 \tag{4}$$

$$\frac{dn_2}{d\tau} \simeq -(N_1\sigma_2 + \gamma_2)n_2 + \gamma_3 n_3 \tag{5}$$

$$\frac{dn_s}{d\tau} = \sigma_{s-1} n_{s-1} N_1 - \sigma_s n_s N_1 + \gamma_{s+1} n_{s+1} - \gamma_s n_s, \tag{6}$$

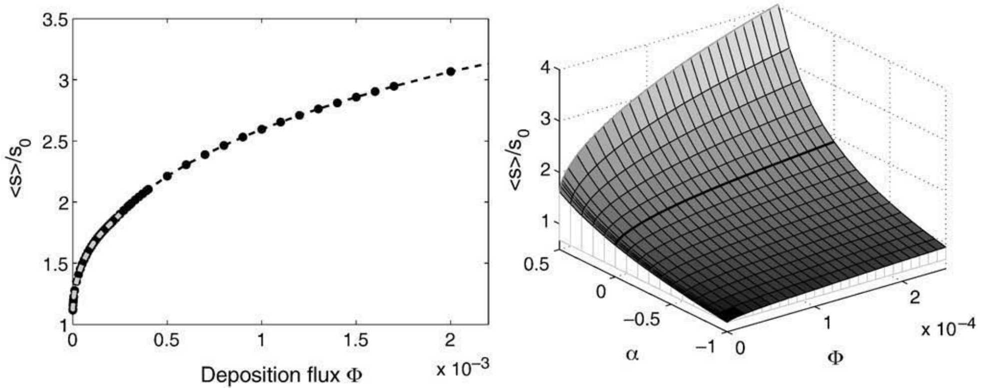

Fig. 1. The mean size of the stationary state, when α is zero (left). Solid dots are simulated stationary states. On the right side is the surface formed by varying the parameter α. The scaling factor s_0 is 2000. Error bars are smaller in magnitude than the size of the solid dots.