Kinetic models of quantum size effect-directed nanocluster self-assembly in atomic corrals

Mikhail Khenner

Department of Mathematics, Western Kentucky University, Bowling Green, KY 42101, United States of America
Applied Physics Institute, Western Kentucky University, Bowling Green, KY 42101, United States of America

E-mail: mikhail.khenner@wku.edu

Received 12 May 2022, revised 22 September 2022
Accepted for publication 13 October 2022
Published 20 October 2022

Abstract
Two simple kinetic models of quantum size effect-directed nanocluster self-assembly in circular atomic corrals are discussed. The models correspond to an adsorption (either a physisorption or a chemisorption) and an adsorption-diffusion regimes that are typical at low and high temperatures, respectively. Small magnitudes of a variation of the electronic local density of states is shown to be the prime factor that impedes self-assembly in the latter regime.

Keywords: quantum size effect, atomic corrals, nanocluster self-assembly, kinetic model

1. Introduction
The scattering of the surface electrons off surface-implanted atoms generates Friedel oscillations on the close-packed surfaces of noble metals, e.g. a standing wave patterns in the electron density (local density of states, or LDOS) [1]. A standing wave pattern is the result of interference of two or more scattered waves. Standing wave patterns can be used to confine adatoms inside quantum corrals built from surface-implanted atoms and thus engineer artificial structures of single adatoms or self-assembled nanoclusters.

Despite that standing wave LDOS patterns on surfaces and a long-range adsorbate interactions mediated by a two-dimensional electron gas are relatively well-understood [1–4], the kinetics of self-assembly driven by standing wave LDOS patterns was not sufficiently studied neither experimentally, nor theoretically. For theoretical support, sometimes an experimental study of self-assembly outcomes is supplemented with a limited Monte-Carlo simulation of adatom diffusion [5–7], but basic questions such as to what extent the geometry of a standing wave LDOS pattern and a magnitude of a spatial variation of LDOS affect self-assembly and its kinetics are left unclarified. In fact, LDOS is seldom constructed and directly appealed to when interpreting experimental outcomes. In this notice, we construct two minimalist models of self-assembly kinetics in order to point out that these factors are crucial.

QSE diminishes with rising temperature, and typically at room temperature it has a vanishingly small effect on self-assembly. However, in some systems [8–12] QSE drives the self-assembly even at room temperature. It was argued that in these systems QSE selectively affects the adsorption properties of the substrate, e.g. it laterally modulates the adsorption, thus the atoms that are deposited onto a strong-adsorption sites bind strongly to the substrate [8, 11]. As clusters of several atoms form, the electronic shell effect of quantum confined electrons may further increase binding of atoms in a cluster and even promote nucleation of ‘magic’ clusters [12]. At room temperature the surface diffusion is not sufficiently strong to dissolve the newly formed clusters. Correspondingly, our models describe a low (high) temperature regime when the kinetics is governed by adsorption (by adsorption and diffusion). We take all required QSE-related material...
parameters directly from [8], where they correspond to Ni adsorbate on Rh(111) substrate. This is for illustration only, as the models can be applied to any adsorbate/substrate pair that produces QSE-directed self-assembly via spatial modulation of adsorption.

Manai et al [8] posits that a standing wave pattern of LDOS modifies the adsorption properties of the surface. The variation of the LDOS (\(\Delta LDOS\)) depends on Fermi wavenumber \(k_F\), the distance \(r_i\) from the \(i\)-th scattering center and the Fermi level phase shift \(\delta\), and is described by the equation [1]:

\[
\Delta LDOS = \sum_{i=1}^{n} \Delta LDOS_i = \sum_{i=1}^{n} \frac{\cos^2(2\pi r_i - \pi/4 + \delta) - \cos^2(2\pi r_i - \pi/4)}{2\pi r_i},
\]

\[
r_i = \sqrt{\left(x-x^{(i)}_c\right)^2 + \left(y-y^{(i)}_c\right)^2}.
\]

Equation (1) states that \(\Delta LDOS\) is the sum of contributions from \(n\) scattering centers (metal atoms) located at \(\left(x^{(i)}_c, y^{(i)}_c\right)\). A maximum in \(\Delta LDOS\) is a potential well and it is a suitable adsorption site. In this paper, the scattering centers are assumed to be equispaced on a circle of radius \(R\) (a corral), thus:

\[
x^{(i)}_c = R \cos \frac{2\pi i}{n}, \quad y^{(i)}_c = R \sin \frac{2\pi i}{n}, \quad i = 1, \ldots, n. \quad (2)
\]

All distances were made non-dimensional with Fermi wavelength \(\lambda_F\). \(\delta = 0.3\) [8] will be used for all \(\Delta LDOS\) computations in this paper.

Figures 1(a) and (b) show \(\Delta LDOS\) in the interior of two corrals of different radii, prepared with \(n = 6\) scattering centers with the angular separation of 60°. Notice that the magnitude of \(\Delta LDOS\), i.e. the difference between \(\Delta LDOS\) maximum and minimum, is two times larger for \(R = 1\) case. This paper we denote the magnitude of \(\Delta LDOS\) as \(M_\Delta\). The expression for \(M_\Delta\) cannot be easily determined from equation (1) even for simple scattering geometries such as corrals made of a handful of atoms. Also, there is no easy or convenient way to analytically find or estimate the number and location of peaks in \(\Delta LDOS\) for given \(\delta\), \(n\) and \(R\). Thus the contour plots such as in figure 1 are the most practical way to quantify \(M_\Delta\) and to determine the landscape of \(\Delta LDOS\).

2. Adsorption modeling (A-model)

We start by assuming that at low temperatures (<300 K) a surface diffusion is negligible in comparison to adsorption. Thus in this section we apply \(\Delta LDOS\) shown in figures 1(a) and (b) to compare the adsorption kinetics inside the corresponding corrals.

Although atomic and molecular adsorption is a complicated and heavily material-dependent phenomenon on a microscopic level [13], the adsorption on a coarse, i.e. mesoscopic, level is typically differentiated into a physisorption and a chemisorption [14]. The prototype kinetics of physisorption is usually modeled by an initial value problem for a first-order ordinary differential equation (ODE IVP) and is known as pseudo-first order (PFO) kinetics [15]. In the context of continuous adsorption that is mediated by \(\Delta LDOS\) this problem reads:

\[
\frac{d\rho}{dt} = A \Delta LDOS (1 - \rho), \quad \rho(x,y,t) = \rho_0(x,y), \quad (3)
\]

where \(\rho(x,y,t)\) is adsorbate coverage in monolayers (0 ≤ \(\rho\) ≤ 1), \(\rho_0(x,y)\) the initial coverage, and \(A\) the dimensionless parameter that quantifies the adsorption strength. Analytical solution of the problem (3) is easily found:

\[
\rho_{pfo} = \rho_0 + A \Delta LDOS (1 - \rho_0) t \quad (4)
\]

Similarly, the prototype ODE IVP for chemisorption kinetics is known as pseudo-second order (PSO) kinetics [15]. For adsorption that is modulated by \(\Delta LDOS\) that problem reads:

\[
\frac{d\rho}{dt} = A \Delta LDOS (1 - \rho)^2, \quad \rho(x,y,0) = \rho_0(x,y). \quad (5)
\]

Its analytical solution is:

\[
\rho_{pso} = \rho_0 + A \Delta LDOS (1 - \rho_0) t \quad (6)
\]

Note that the time \(t\) is dimensionless in equations (3)–(6).

For consistency with the adsorption-diffusion model (A+D model, section 3), the physical time was adimensionalized by the same scale as in section 3, i.e. \(t = t_\infty / (\nu D^{2/3})\), where \(D\) is the surface diffusion coefficient of an adsorbate, \(\nu\) the aortal density of adsorption sites, and \(S = \pi d^2/4\) the area of an adsorbate atom cross-section (with \(d\) the diameter of an adsorbate atom), \(t = 4 \times 10^{-6} \) at the typical values \(\lambda_F = 2\pi/k_F = 0.9 \text{ nm}\) (corresponding to \(k_F = 0.7 \text{ Å}^{-1}\) [8]), \(\nu = 5 \times 10^{14} \text{ cm}^2/\text{s}\), \(D = 10^{-8} \text{ cm}^2/\text{s}\) (at \(T = 300 \text{ K}\)), \(S = 8.35 \times 10^{-16} \text{ cm}^2\) (corresponding to \(d = 0.326 \text{ nm}\) of Ni atom). Thus \(A\) was chosen of similar magnitude, \(A = 10^{-6}\), and the solutions \(\rho_{pfo}\) and \(\rho_{pso}\) were evaluated to \(t \sim 2 \times 10^7\), which corresponds to a physical time about 80 s (see figure 2).

From equations (4) and (6) it is easy to notice that for any positive \(A\) and \(\Delta LDOS\), \(\rho_{pfo}\) and \(\rho_{pso}\) approach one (the complete monolayer coverage) as \(t\) tends to infinity, albeit the kinetic laws are different and the exact kinetics should be sensitive to \(M_\Delta\) and, to a lesser degree, to (spatial) variations of \(\Delta LDOS\). In figure 2 these differences are quantified. Compared to PSO, PFO adsorption kinetics establishes the maximum spatial difference of the coverage and the median value of the coverage over the substrate area inside a corral more

---

1 We consider small corrals (both size-wise and atoms-wise) in order to compute \(\Delta LDOS\) and adsorbate coverage with high accuracy.

2 From equation (1) it is obvious that \(\Delta LDOS\) takes on negative values at some points \((x,y)\). For uniformity, we shift all computed \(\Delta LDOS\) into a positive range by a pointwise addition of a constant \(\min(\Delta LDOS)\), where the minimum is computed over all points inside a disk (see figures 1 and 7). Such shifts by a constant do not affect any results, but they simplify the comparisons of various \(\Delta LDOS\).
Figure 1. $\Delta$LDOS in the interior of a six-atoms corral. The atoms (scatterers) themselves, and $\Delta$LDOS in their immediate vicinity are not shown. (a) $R = 1$. (b) $R = 2$. Note from the color bars that $M_\Delta \approx 1$ in (a), $M_\Delta \approx 0.5$ in (b). For comparison with (b), $\Delta$LDOS in the interior of a four, eight and twelve-atoms corrals of the same radius is shown in figure 7.

Figure 2. A-model: comparison of adsorption kinetics for the six-atoms corral with $\Delta$LDOS in figure 1(b). (a) $\rho_{\text{max}} - \rho_{\text{min}}$, PSO. Fit: $0.547 \arctan (6.903t)$. (b) $\rho_{\text{max}} - \rho_{\text{min}}$, PFO. Fit: $0.634 \arctan (8.146t)$. (c) Median $\rho$, PSO. Fit: $0.330 \arctan (10.272t)$. (d) Median $\rho$, PFO. Fit: $0.369 \arctan (9.969t)$.

than twice faster. Because of faster kinetics, the final values of these quantities at $t = 2 \times 10^7$ for PFO case are 15% larger than the corresponding values for PSO case.

The snapshots of $\rho_{\text{PSO}}$ evolution are shown in figures 3 and 4; we omit similar looking figures for $\rho_{\text{PFO}}$. It is seen that the atoms preferentially adsorb at the areas of the substrate where $\Delta$LDOS is maximized in figures 1(a) and (b). These regions are associated with a self-assembled nanoclusters, whose size increases with time. At $t = 2 \times 10^7$ the nanocluster formation is complete ($\rho_{\text{PSO}} \sim 1$, i.e. a monolayer coverage is locally reached).

3. Adsorption and diffusion modeling (A+D-model)

At temperatures above room temperature both adsorption and surface diffusion are operative. The coverage evolves according to the following dimensionless partial differential equation:

$$
\frac{\partial \rho}{\partial t} = A \Delta \text{LDOS} \left(1 - \rho\right)^k + \nabla^2 \rho + \nabla \cdot J,
$$

$$
\rho(x,y,0) = \rho_0(x,y), \quad k = 1,2
$$

$$
J = (\nu S)^{-1} B \rho \left(1 - \rho\right) \nabla \rho.
$$

(7)
Figure 3. $A$-model: $\rho_{\text{PSO}}$ at the increasing times for the six-atoms corral with $\Delta \text{LDOS}$ in figure 1(a). (a) $t = 0$, (b) $t = 2500$, (c) $t = 10^4$, (d) $t = 10^6$, (e) $t = 2 \times 10^7$.

Figure 4. $A$-model: $\rho_{\text{PSO}}$ at the increasing times for the six-atoms corral with $\Delta \text{LDOS}$ in figure 1(b). (a) $t = 0$, (b) $t = 2500$, (c) $t = 10^4$, (d) $t = 10^6$, (e) $t = 2 \times 10^7$.

The diffusion parts of equation (7), i.e. the second and the third terms at the right-hand side, were derived from a law of mass conservation [16]. The exponent $k = 1$ ($k = 2$) in the adsorption term stands for PFO (PSO) adsorption kinetics, $J$ is the component of the diffusion flux that emerges due to lateral adsorbate-adsorbate interactions, and:

$$|B| = \frac{\beta_1 + \beta_2}{kT}$$  \hspace{1cm} (8)

is the dimensionless magnitude of these interactions. Equation (7) necessitates a numerical solution.
ical collision of the atoms. For Ni the potential. At
adsorbate \[ \text{of the attractive-repulsive potential for the atoms of an} \]
sine and cosine integral functions. For Ni where,
\( \beta \)
Figure 5. \( A + D \) model: \( \rho_{pso} \) at the increasing times for the six-atoms corral with \( \Delta LDOS \) in figure 1(a). (a) \( t = 10^5 \), (b) \( t = 2 \times 10^5 \), (c) \( t = 1.5 \times 10^5 \).

Figure 6. \( A + D \) model: \( \rho_{pso} \) at the increasing times for the six-atoms corral with \( \Delta LDOS \) in figure 1(b). (a) \( t = 10^5 \), (b) \( t = 7 \times 10^5 \), (c) \( t = 2.5 \times 10^5 \).

The first term in the numerator of \( B \) is the first moment of the Friedel interaction potential \( U_F \) of two adsorbate atoms separated by a distance \( r \) \([2–4, 8]\) (recall, that all distances are made dimensionless using \( \lambda_F \) as the length scale):

\[
\beta_1 = - \int_a^\infty U_F(r) \, dr = -E_F \left( \frac{2 \sin \delta}{\pi} \right)^2 \int_a^\infty \frac{\sin 2(2\pi r + \delta)}{(2\pi r)^2} \, dr
\]

\[
= \frac{-2E_F \sin^2 \delta}{\pi^2} \left[ 2 \sin(2\delta) \, \text{Si}(4\pi a) - 2 \cos(2\delta) \, \text{Ci}(4\pi a) \right.
\]

\[
\left. - \pi \sin 2\delta + \frac{\sin 2(\delta + 2\pi a)}{2\pi a} \right], \quad (9)
\]

where, \( a \) is the (dimensionless) lattice spacing of the adsorbate, \( \text{Si}(z) = -\int_z^\infty \sin(t)/t \, dt \) and \( \text{Ci}(z) = -\int_z^\infty \cos(t)/t \, dt \) are the sine and cosine integral functions. For Ni \( a = 0.277 \) and \( E_F = 5.01 \ eV \) \([18]\).

The second term in the numerator of \( B \) is the first moment of the attractive-repulsive potential for the atoms of an adsorbate \([17]\):

\[
\beta_2 = - \int_a^\infty U_{5c}(r) \, dr = -\epsilon \int_a^\infty \left( \frac{a}{r} \right)^n - 2\epsilon \left( \frac{a}{r} \right)^{m/2} \right] \, dr
\]

\[
= \epsilon a \left( \frac{1}{n-1} + \frac{2\epsilon}{1 - m/2} \right), \quad (10)
\]

where \( \epsilon \) is the magnitude of \( U_{5c}(r) \) with the dimension of energy, and \( c, m \) and \( n \) are the dimensionless parameters of the potential. At \( n > m \), \( U_{5c}(r) \) is attractive at long distances and repulsive at very short distances, preventing the unphysical collision of the atoms. For Ni \( \epsilon = 0.016 \ eV, \ c = 39.426, \ m = 7, \) and \( n = 9 \) \([17]\). As evaluated, \( \beta_1, \ \beta_2 < 0 \) and they have similar magnitudes, \( |\beta_1| \sim |\beta_2| \sim 0.006 \ eV \).

To illustrate how the surface diffusion interferes with \( \Delta LDOS \)-mediated adsorption inside the corrals, figures 5 and 6 show the evolution of \( \rho_{pso} \) computed using equation (7) with \( \Delta LDOS \) in figures 1(a) and (b), i.e. for the small and large six-atoms corrals. These results should be compared to figures 3 and 4 that show a nanocluster self-assembly inside these corrals due only to \( \Delta LDOS \)-mediated adsorption. (The initial condition \( \rho(x, y, 0) = \rho_0(x, y) \) is the same for the computations of \( A \)-model and \( A + D \) model.) It is seen that the median coverage still increases due to continuous adsorption but diffusion, as expected, makes \( \rho_{\text{max}} - \rho_{\text{min}} \), close to negligible. Note however, that the footprint of \( \Delta LDOS \)-mediated adsorption remains in figure 5, but it is gone in figure 6. Microscopically, a nanoclusters comprised of a few atoms are expected to form at the locations of \( \Delta LDOS \) maxima inside the smaller corral of radius one, but they are not expected to form inside the larger corral of radius two. This crucial difference can be attributed only to larger \( M_\Delta \) for \( \Delta LDOS \) in figure 1(a).

To further support this conclusion, in figure 7 we show \( \Delta LDOS \) in the interior of three circular corrals of radius two. The corrals are prepared with four, eight, and twelve scattering centers that are equipspaced on the corral’s boundary \( (\pi/2, \pi/4, \) and \( \pi/6 \) angular separation between the centers). \( M_\Delta \) increases from \( \approx 0.5 \) to \( \approx 0.9 \) as the number of scattering centers increases. Note that for four and six scattering centers \( M_\Delta \) values are very close, see figure 1(b). It follows that \( M_\Delta \) is a monotonically increasing function of the number of scattering centers (at least for the corral of radius two). We computed
evolution of $\rho_{ps\sigma}$ inside these corrals using $A + D$ model. For the eight and twelve-atoms corrals that produce larger $M_\Delta$ in $\Delta$LDOS, the coverage evolution is qualitatively similar to one shown in figure 5; for the twelve-atoms corral the evolution is shown in figure 8. Nanocluster self-assembly inside these corrals is therefore expected. For the four-atoms corral that produces small $M_\Delta$ in $\Delta$LDOS, the coverage evolution is qualitatively similar to one shown in figure 6. Nanocluster self-assembly inside this corral is not expected. Thus it follows that there exists a threshold value of $M_\Delta$ around 0.7 below which $\Delta$LDOS-mediated adsorption loses a competition with diffusion and thus it cannot sustain a nanocluster formation inside the corrals.

4. Conclusions

We formulated the adsorption and the adsorption-diffusion kinetic models for the QSE-directed nanocluster self-assembly inside a circular corrals built up of metal atoms that act as scattering centers for the surface electrons. In our minimalist modeling, once $\Delta$LDOS is fixed by selecting an adsorbate, a substrate, a corral radius and the number of atoms on a corral boundary, the self-assembly kinetics is governed by only one dimensionless parameter (the adsorption model) or two dimensionless parameters (the adsorption-diffusion model). These parameters are the adsorption rate and the strength of lateral adsorbate-adsorbate interactions. The models show that when surface diffusion is significant, as is the case when temperature is high, a self-assembly is sustained only inside those corrals that exhibit an above-threshold value of $\Delta$LDOS magnitude. Computations such as performed in this paper may be a useful tool for designing corrals that guide a nanocluster self-assembly via the electronic quantum size effects.

The described $A + D$ model may be tuned and made more quantitative, for instance, by ascribing a temperature dependence to the adsorption strength $A$. Rather than assuming such dependence based on general considerations, it would be more useful to extract it from the experiment data for a specific adsorbate/substrate system. (Likewise, a surface diffusion coefficient $D$ should be taken in the Arrhenius form, where the activation energy and the pre-factor are material system-specific.) Unfortunately, we were unable to find an account of an experiment done at different temperatures. Thus a detailed investigation is postponed until such data becomes available.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID ID

Mikhail Khenner ORCID: https://orcid.org/0000-0002-6398-8437
References

[1] Crommie M F, Lutz C P and Eigler D M 1993 Confinement of electrons to quantum corrals on a metal surface Science 262 218

[2] Knorr N, Brune H, Eppe M, Hirstein A, Schneider M A and Kern K 2002 Long-range adsorbate interactions mediated by a two-dimensional electron gas Phys. Rev. B 65 115420

[3] Repp J, Moresco F, Meyer G, Rieder K-H, Hyldgaard P and Persson M 2000 Substrate mediated long-range oscillatory interaction between adatoms: Cu/Cu(111) Phys. Rev. Lett. 85 2981

[4] Hyldgaard P and Persson M 2000 Long-ranged adsorbate–adsorbate interactions mediated by a surface-state band J. Phys.: Condens. Matter 12 L13–L19

[5] Cao R X, Miao B F, Zhong Z F, Sun L, You B, Zhang W, Wu D, Hu A, Bader S D and Ding H F 2013 Two-dimensional quantum diffusion of Gd adatoms in nano-size Fe corrals Phys. Rev. B 87 085415

[6] Li Q, Cao R and Ding H 2020 Quantum size effect in nanocorrals: from fundamental to potential applications Appl. Phys. Lett. 117 060501

[7] Stepanyuk V S, Negulyaev N N, Niebergall L, Longo R C and Bruno P 2006 Adatom self-organization induced by quantum confinement of surface electrons Phys. Rev. Lett. 97 186403

[8] Manai G, Radican K, Delogu F and Shvets I V 2008 Room-temperature self-assembly of equilateral triangular clusters via friedel oscillations Phys. Rev. Lett. 101 165701

[9] Kidd T E, Scott S, Roberts S, Carlile R, Lukashev P V and Stollenwerk A J 2021 Electronic growth of Pd(111) nanostructures on MoS2 J. Appl. Phys. 129 174303

[10] Kidd T E, Weber J, Holzapfel R, Doore K and Stollenwerk A J 2018 Three-dimensional quantum size effects on the growth of Au islands on MoS2 Appl. Phys. Lett. 113 191603

[11] Jiang P, Ma X, Ning Y, Song C, Chen X, Jia J-F and Xue Q-K 2008 Quantum size effect directed selective self-assembling of cobalt phthalocyanine on Pb(111) thin films J. Am. Chem. Soc. 130 7790–1

[12] Gwo S, Chou C-P, Wu C-L, Ye Y-J, Tsai S-J, Lin W-C and Lin M-T 2003 Self-limiting size distribution of supported cobalt nanoclusters at room temperature Phys. Rev. Lett. 90 185506

[13] Liu X, Wang C Z, Hupalo M, Lu W C, Tringides M C, Yao Y X and Hoa K M 2012 Metals on graphene: correlation between adatom adsorption behavior and growth morphology Phys. Chem. Chem. Phys. 14 9157–66

[14] Lüth H 2010 Solid Surfaces, Interfaces and Thin Films 5th edn (Berlin: Springer)

[15] Azizian S 2004 Kinetic models of sorption: a theoretical analysis J. Colloid Interface Sci. 276 47–52

[16] Khenner M and Hebenstiel L 2021 A mesoscopic model of nanoclusters self-assembly on a graphene Moiré J. Appl. Phys. 130 124301

[17] Sutton A P and Chen J 1990 Long-range Finnis–Sinclair potentials Phil. Mag. Lett. 61 139

[18] Ehrenreich H, Philipp H R and Olechta D J 1963 Optical properties and fermi surface of nickel Phys. Rev. 131 2469