Directing Anisotropic Assembly of Metallic Nanoclusters by Exploiting Linear Trio Interactions and Quantum Size Effects: Au Chains on Ag(100) Thin Films

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Abstract
Discovery and understanding of mechanisms for kinetically controlled growth of metal nanoclusters can be enabled by realistic atomistic-level modeling with ab initio kinetics. KMC simulation of such a model for Au deposition on Ag(100) films reveals the formation of single-atom-wide Au chains below 275 K, even though 2D islands are thermodynamically preferred. Chain formation is shown to reflect a combination of strong linear trio attractions guiding assembly and a weak driving force and slow rate of transformation of 1D chains to 2D islands (or sometimes irreversible rounding of adatoms from chain sides to ends). Behavior can also be tuned by quantum size effects: chain formation predominates on 2-monolayer Ag(100) films supported on NiAl(100) at 250 K for low coverages but not on 1- or 3-monolayer films, and longer chains form than on bulk Ag(100). Our predictive kinetic modeling shows the potential for simulation-guided discovery and analysis of novel self-assembly processes.

Keywords
self-assembly, Au chains, ab initio periphery diffusion kinetics, KMC simulation

Disciplines
Astrophysics and Astronomy | Chemistry

Comments
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Supporting Information

ABSTRACT: Discovery and understanding of mechanisms for kinetically controlled growth of metal nanoclusters can be enabled by realistic atomistic-level modeling with ab initio kinetics. KMC simulation of such a model for Au deposition on Ag(100) films reveals the formation of single-atom-wide Au chains below 275 K, even though 2D islands are thermodynamically preferred. Chain formation is shown to reflect a combination of strong linear trio attractions guiding assembly and a weak driving force and slow rate of transformation of 1D chains to 2D islands (or sometimes irreversible rounding of adatoms from chain sides to ends). Behavior can also be tuned by quantum size effects: chain formation predominates on 2-monolayer Ag(100) films supported on NiAl(100) at 250 K for low coverages but not on 1- or 3-monolayer films, and longer chains form than on bulk Ag(100). Our predictive kinetic modeling shows the potential for simulation-guided discovery and analysis of novel self-assembly processes.

Dramatic advances have been achieved in the experimental control of nonequilibrium shapes during the synthesis of metallic nanocrystals or nanoclusters (NCs). These shapes strongly impact, for example, catalytic or plasmonic properties. NC self-assembly via solution-phase synthesis or via deposition onto smooth surfaces can produce: 3D NCs with spherical, polyhedral, or other shapes (which are truncated for supported NCs); 2D platelets in solution or monolayer islands on surfaces; and 1D NC rods, wires, or chains. For solution-phase synthesis, a substantial heuristic understanding has been developed for these kinetically controlled shapes accounting for, for example, the effect of capping agents on facet energies and growth kinetics and the role of inhibited perimeter diffusion; however, such synthesis is still regarded as art versus science, and detailed molecular-level understanding is lacking. For assembly of epitaxial NCs on crystalline surfaces, a more detailed understanding has been achieved via atomistic lattice-gas modeling and kinetic Monte Carlo (KMC) simulation. Here there is an appreciation that the finer details of perimeter diffusion, such as inlet kink rounding, step edge crossing, or interfacet transport, strongly impact shape. Initial misperceptions regarding factors inducing nonequilibrium dendritic shapes, elongated shapes, and the subtle effect on shape of additives decorating the NC periphery were corrected as a result of such modeling.

Our focus in this study is on anisotropic NC shapes familiar for Au, Ag, and other metals. Specifically, we consider diffusion-mediated self-assembly of epitaxial Au NCs by deposition onto metal surfaces. Nanowires are often formed by deposition onto anisotropic metal or semiconductor surfaces or onto vicinal surfaces where steps direct assembly. However, we will demonstrate an alternative strategy that exploits many-body adatom interactions, anticipating that linear trio attractions could induce the formation of atomic chains even on isotropic surfaces. Although many-body interactions are generally weak, we show that they are significant for Au and can be tuned (together with other key energetics) by exploiting quantum size effects (QSEs) to facilitate anisotropic assembly. QSE in supported metal films of a few monolayers is associated with electron confinement, the variation of energetics reflecting commensurability of the Fermi wavelength with nanoscale film thickness. Prominent examples of the influence of QSEs include the formation of ultraflat deposited Ag films and tunable nucleation, reaction, and oxidation kinetics on thin metal films.

An obstacle to experimental identification of optimal surface systems for anisotropic assembly guided by many-body interactions and QSE is the many possible combinations of deposited atoms, metallic thin films, and supports. Thus, a capability for predictive atomistic-level modeling would greatly facilitate simulation-guided discovery of appropriate systems. However, a challenge for such modeling is the need to precisely describe both system thermodynamics and also distinct barriers for terrace diffusion and for edge diffusion and corner rounding for all relevant edge configurations (barriers to which NC

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formation is exquisitely sensitive). We implement a procedure described below to obtain such barriers at the level of ab initio density functional theory (DFT). These provide precise input for KMC simulation of the NC assembly processes on the physical time scale. The Supporting Information (SI) provides details of our DFT and KMC analyses.

Another challenge is that most DFT analyses of thin films consider unsupported slabs due to both computational efficiency and uncertainty regarding the film-support interface; however, predictive modeling requires more demanding analysis for supported films with correct interface structure. Thus, while performing efficient exploratory analysis for unsupported slabs, we focus on judiciously selected supported thin film systems with known interface structure. In addition, we select a low-strain system as approaches for edge diffusion barriers for edge diode adatoms, which are further enhanced by QSE for Ag(100) thin films, respectively (with $\phi_{21}$/2 highest for 3–4 ML slabs). KMC simulations show that these strong $\phi_{21}$ values are associated with the formation of single-atom-wide chains at 250 K, more prominently on a 4-ML slab than bulk Ag(100); see Figure 1ab.

Behavior for supported films generally differs from that for unsupported slabs due to strain (absent for Au/Ag/NilAl(100)), differing chemical environments (a minor effect for 2–2 ML films), and QSE. Electron confinement in metal-on-metal films, depolarization of the free-standing Ag(100) slabs versus thickness show the same trends for $E_{TS}$, $E_{1D}$, and $E_{2D}$ (see SI). Furthermore, $\phi_{21}$ is enhanced due to QSE in thin Ag(100) slabs: $\phi_{21} = -0.069$, $-0.088$, $-0.102$, and $-0.087$ eV compared with $\phi_{21} = -0.164$, $-0.111$, $-0.121$, and $-0.197$ eV for 2–5 ML Ag(100) slabs, respectively (with $\phi_{21}$/2 highest for 3–4 ML slabs). KMC simulations show that these strong $\phi_{21}$ values guide the formation of single-atom-wide chains at 250 K, more prominently on a 4-ML slab than bulk Ag(100); see Figure 1ab.

As a preliminary analysis, we assess $\omega$ interactions for Au on bulk Ag(100) and the dependence on thickness for freestanding Ag(100) slabs. For bulk Ag(100), the linear trio attraction $\omega_{T1} = -0.065$ eV is unusually strong relative to the NN pair attraction $\omega_{T1} = -0.201$ eV ($\sim$30% versus the typical $\sim$10%). Furthermore, $\omega_{T1}$ is enhanced due to QSE in thin Ag(100) slabs: $\omega_{T1} = -0.069$, $-0.088$, $-0.102$, and $-0.087$ eV compared with $\omega_{T1} = -0.164$, $-0.111$, $-0.121$, and $-0.197$ eV for 2–5 ML Ag(100) slabs, respectively (with $\omega_{T1}$/2 highest for 3–4 ML slabs). KMC simulations show that these strong $\omega_{T1}$ do guide the formation of single-atom-wide chains at 250 K, more prominently on a 4-ML slab than bulk Ag(100); see Figure 1ab.

Behavior for supported films generally differs from that for unsupported slabs due to strain (absent for Au/Ag/NilAl(100)), differing chemical environments (a minor effect for 2–2 ML films), and QSE. Electron confinement in metal-on-metal films, a requirement for QSE, can still occur due to a gap or pseudo gap in the normal direction or just a depletion in the density of states near the Fermi level (as expected for NilAl); however, one expects a “phase shift” in the variation of energetics with thickness relative to that for a freestanding slab. Different boundary conditions for the electron wave functions at the film-substrate versus the film-vacuum interface produce this shift. We have performed computationally demanding DFT analyses of energetics for Ag(100) films on Al-terminated NilAl(100). Indeed, curves for $\omega$ versus thickness show the same trends for Ag(100) slabs and supported films but are shifted relative to each other by 1 to 2 ML. See SI Figure 1. Simulated island and

### Scheme 1. Conventional ($\omega$) and Unconventional ($\phi$) Interactions between Au Adatoms Incorporated into KMC Simulations

![Scheme 1](image-url)
chain distributions are shown in Figure 1c–e for Au deposition at 250 K on 1–3 ML supported Ag(100) films. Short chains form in all systems at 0.01–0.02 ML; however, by 0.04 ML, prominent formation of longer chains occurs only for 2-ML supported films, with a tendency to form 2D islands on 1- and 3-ML films. This behavior does not simply correlate with the strength of \( \omega_T \).

One can also assess the \( T \) dependence of self-assembly. For sufficiently high \( T \), thermodynamics should dominate producing 2D islands. For lower \( T \), inhibited terrace diffusion should limit chain length or 2D island size. These expectations are confirmed by the KMC simulation results shown in Figure 2 for 2-ML supported films and bulk Ag(100). In both cases, 2D islands dominate at 275 K. Chain length grows upon increasing \( T \) from 225 to 250 K, especially for 2-ML supported films where 2D islands also form at 250 K.

To provide a deeper understanding of the essential features controlling chain self-assembly, we now go beyond just reporting KMC results to dissect the kinetics of key processes controlling behavior.

**Chain End-to-Side Edge Diffusion.** Previous studies of chain formation on anisotropic fcc(110) surfaces suggested that a key factor is anisotropic corner rounding (facile edge diffusion from chain sides-to-ends and inhibited diffusion from ends-to-sides) and inhibited detachment from chain ends (thereby blocking reattachment on sides).\(^8,29,30\) Earlier studies incorrectly identified anisotropic terrace diffusion as key.\(^7\) Thus, here we characterize edge diffusion in Figure 3a and Table 2. The barrier, \( E_{es} \), for diffusion along chain sides is always much lower than \( E_{de} \) and the barrier, \( E_{se} \), for side-to-end rounding is much lower than that for end-to-side rounding, \( E_{es} \). Thus, corner rounding is anisotropic. Of particular relevance is the rate for the slowest end-to-side rounding process, \( h_{se} = \nu_e \exp(-E_{se}/k_B T) \) relative to the typical rate \( k_{agg} = F/N_{ch} \) for aggregation of deposited adatoms with individual chains for chain density \( N_{ch} \). Naturally, \( k_{agg} \) will exceed \( h_{se} \) at the onset of deposition where

<table>
<thead>
<tr>
<th>( 1 \text{ ML}/\text{NiAl} )</th>
<th>( 2 \text{ ML}/\text{NiAl} )</th>
<th>( 3 \text{ ML}/\text{NiAl} )</th>
<th>( 4 \text{ ML} )</th>
<th>( \infty \text{ ML (bulk)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_{T1} )</td>
<td>-0.276</td>
<td>-0.131</td>
<td>-0.183</td>
<td>-0.121</td>
</tr>
<tr>
<td>( \omega_{T2} )</td>
<td>0.006</td>
<td>+0.052</td>
<td>+0.047</td>
<td>+0.071</td>
</tr>
<tr>
<td>( \omega_{T1e} )</td>
<td>-0.103</td>
<td>-0.115</td>
<td>-0.104</td>
<td>-0.102</td>
</tr>
<tr>
<td>( \omega_{T2e} )</td>
<td>+0.062</td>
<td>+0.011</td>
<td>+0.011</td>
<td>-0.001</td>
</tr>
<tr>
<td>( \phi_{T1} )</td>
<td>-0.335</td>
<td>-0.237</td>
<td>-0.211</td>
<td>-0.130</td>
</tr>
<tr>
<td>( \phi_{T2} )</td>
<td>+0.244</td>
<td>+0.105</td>
<td>+0.100</td>
<td>+0.078</td>
</tr>
<tr>
<td>( \phi_{T3} )</td>
<td>+0.043</td>
<td>-0.013</td>
<td>-0.032</td>
<td>-0.031</td>
</tr>
<tr>
<td>( \phi_{T4} )</td>
<td>-0.055</td>
<td>-0.056</td>
<td>-0.073</td>
<td>-0.086</td>
</tr>
</tbody>
</table>

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![Figure 1](URL)  
**Figure 1.** KMC simulations for Au island and chain formation by Au deposition at 250 K on: (a) bulk Ag(100); (b) 4-ML Ag(100) slab; and (c–e) 1–3 ML Ag(100) supported on Al-terminated NiAl(100) at Au coverages of 0.02 and 0.04 ML. Image size: 28.9 × 28.9 nm².

![Figure 2](URL)  
**Figure 2.** KMC simulations for Au island and chain formation by Au deposition at three different temperatures (225, 250, and 275 K) on (a) bulk Ag(100) and (b) 2-ML Ag(100) thin film supported by Al-terminated NiAl(100) at Au coverage of 0.05 ML. Image size: 28.9 × 28.9 nm².

![Figure 3](URL)  
**Figure 3.** (a) Adsorption site and TS energies around the periphery of an Au chain. Atom-tracking KMC results for Au deposition with yellow (red) atoms deposited first (second) on: (b) 2-ML Ag(100) film supported by Al-terminated NiAl(100) and (c) bulk Ag(100).
detachment from chain ends, rounding is facile on the time scale of chain growth. In contrast, the chain transforms to hybrid 1D is convenient to consider a simplification complex space of possible nanocluster configurations where $n$ is large. This transformation involves stochastic evolution in the thermodynamically preferred 2D islands? supported films (and for freestanding slabs), the rate for the slowest end-to-side rounding process, $h_{det}$, at 250 K, is well above the typical $k_{agg} \approx 1.5 \times 10^9$ site at coverage 0.04–0.1 ML with $F = 0.006$ ML/s. Thus, end-to-side rounding is facile on the time scale of chain growth. In contrast, this is not the case for Au on bulk Ag(100). Finally, the rate for detachment from chain ends, $h_{det} = \exp(-E_{det}/k_BT)$ with $E_{det} = E_0 - \omega p_1 - \omega c_1$ (well above $E_{agg}$), is always very low on the time scale of deposition, so this process is inactive.

Additional insight comes from “atom tracking” KMC.29,31 See Figure 3b,c. Here initially deposited Au atoms are colored yellow and subsequently deposited atoms are red. With no detachment or end-to-corner rounding, the center of chains would be yellow and the ends red; however, simulations for 2-ML supported films reveal color mixing. This reflects active end-to-side rounding: earlier deposited yellow atoms leave ends, just aggregated red atoms then join ends, and the gold atoms subsequently rejoin the end by side-to-end rounding. We find significantly less color mixing for Au deposition on bulk Ag(100) consistent with irreversible side-to-end rounding.

To summarize, Au chain formation on bulk Ag(100) derives from effectively irreversible side-to-end rounding ($E_{agg} = 0.643$ eV) and negligible detachment from chain ends ($h_{det} = 0.796$ eV). For other systems, end-to-side rounding is facile (but not end detachment) except for very low coverage, and we propose that differing behavior partly derives from differing driving forces, $\Delta E_{1D-2D} = E_{2D} - E_{1D}$ for the formation of 2D islands from 1D chains; see Table 2. Specifically, those cases with the most prominent chain formation have the weakest driving force, but because end-to-side rounding is facile for 1-ML supported films, how can chains survive conversion to thermodynamically preferred 2D islands?

Table 2. Top Rows Report Key Barriers for Terrace ($E_d$), Straight Edge ($E_s$), End-to-Side ($E_{agg}$), Side-to-End ($E_{det}$) Diffusion, and Detachment from Chain Ends ($E_{det}$)\(^*\)

<table>
<thead>
<tr>
<th></th>
<th>1 ML/NiAl</th>
<th>2 ML/NiAl</th>
<th>3 ML/NiAl</th>
<th>4 ML</th>
<th>$\infty$ ML (bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_d$</td>
<td>0.449</td>
<td>0.553</td>
<td>0.501</td>
<td>0.515</td>
<td>0.530</td>
</tr>
<tr>
<td>$E_s = E_d - E_d$</td>
<td>0.261</td>
<td>0.267</td>
<td>0.276</td>
<td>0.394</td>
<td>0.437</td>
</tr>
<tr>
<td>$E_{agg} = E_d - E_s$</td>
<td>0.536</td>
<td>0.459</td>
<td>0.545</td>
<td>0.577</td>
<td>0.643</td>
</tr>
<tr>
<td>$E_{det} = E_d - E_s$</td>
<td>0.371</td>
<td>0.423</td>
<td>0.430</td>
<td>0.476</td>
<td>0.562</td>
</tr>
<tr>
<td>$\epsilon_i \equiv \Delta E_{1D-2D}$</td>
<td>-0.143</td>
<td>-0.098</td>
<td>-0.149</td>
<td>-0.085</td>
<td>-0.142</td>
</tr>
<tr>
<td>$\epsilon_1$</td>
<td>-0.080</td>
<td>+0.034</td>
<td>-0.090</td>
<td>+0.034</td>
<td>-0.154</td>
</tr>
<tr>
<td>$\epsilon_0 \equiv \Delta E_{agg}$</td>
<td>+0.222</td>
<td>+0.310</td>
<td>+0.221</td>
<td>+0.291</td>
<td>+0.099</td>
</tr>
</tbody>
</table>

\(^*\)Lower rows relate to the energy cost $\Delta E_{agg} = \epsilon_0 + (n-2)\epsilon_1 + (n-2)^2\epsilon_2$ to shift $n(n-1)$ atoms from the chain end to the side, creating an $n \times n$ square at the chain end. Note that $\epsilon_0 \equiv \Delta E_{1D-2D} \equiv E_{2D} - E_{1D}$ gives the preference for 2D islands over 1D chains, and $\epsilon_0 \equiv \Delta E_{agg}$ gives the energy cost for a creating a 2 $\times$ 2 square at the chain end. For meanings of $E_1$, $E_s$, $E_{agg}$, and $E_{det}$ see Figure 3a.

$N_{ch}$ is low, so edge-to-side rounding is effectively irreversible promoting initial chain formation; however, for 1–3 ML supported films (and for freestanding slabs), the rate for the slowest end-to-side rounding process, $h_{det}$, at 250 K, is well above the typical $k_{agg} \approx 1.5 \times 10^9$ site at coverage 0.04–0.1 ML with $F = 0.006$ ML/s. Thus, end-to-side rounding is facile on the time scale of chain growth. In contrast, this is not the case for Au on bulk Ag(100). Finally, the rate for detachment from chain ends, $h_{det} = \exp(-E_{det}/k_BT)$ with $E_{det} = E_0 - \omega p_1 - \omega c_1$ (well above $E_{agg}$), is always very low on the time scale of deposition, so this process is inactive.

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To summarize, Au chain formation on bulk Ag(100) derives from effectively irreversible side-to-end rounding ($E_{agg} = 0.643$ eV) and negligible detachment from chain ends ($h_{det} = 0.796$ eV). For other systems, end-to-side rounding is facile (but not end detachment) except for very low coverage, and we propose that differing behavior partly derives from differing driving forces, $\Delta E_{1D-2D} = E_{2D} - E_{1D}$ for the formation of 2D islands from 1D chains; see Table 2. Specifically, those cases with the most prominent chain formation have the weakest driving force, but because end-to-side rounding is facile for 1-ML supported films, how can chains survive conversion to thermodynamically preferred 2D islands?

Transformation from 1D Chains to 2D Islands. Chain survival when end-to-side rounding is facile must reflect the feature that there is a significant effective barrier for the transformation of 1D chains into hybrid 1D-2D structures and finally into 2D islands. This transformation involves stochastic evolution in the complex space of possible nanocluster configurations. Thus, it is convenient to consider a simplified scenario wherein a long chain transforms to hybrid 1D–2D structures,\(^{m}\), by moving various numbers, $m$, of atoms from one end to one side (so $m$ is the “reaction coordinate”). The energy cost, $\Delta E_{m}$, increases from $\Delta E_{m} = 0$ over the effective barrier before decreasing like $\Delta E_{m} \propto m\Delta E_{1D-2D} < 0$, for large $m$. Larger $\Delta E_{1D-2D}$ makes it more likely that the “biased walk” through configuration space will evolve to a 2D island versus returning to the chain. To concretely illustrate this behavior, consider the special subset of configurations where $m = n(n-1)$ atoms at the end of a long chain are moved to form an $n \times n$ square located at the end of the chain; see Figure 4a. One can show that $\Delta E_{m} = \Delta E_{agg} = \epsilon_0 + (n-2)\epsilon_1 + (n-2)^2\epsilon_2$, for $n \geq 2$

where $\epsilon_i \equiv \Delta E_{1D-2D} = \omega p_1 + 3\omega p_2 - 2\omega_1 + 5\omega_2, \epsilon_1 = 2\omega_1 + 4\omega_2 + 8\omega_2, \epsilon_2 = 2\omega_1 + 4\omega_2 + 8\omega_2$. The variation of $\Delta E_{m}$ with $n$ for supported films is shown in Figure 4b and mimics classic 2D nucleation theory.32 From Table 2, it is clear that $\Delta E_{m} = \Delta E_{agg}$ both increases most strongly from $\Delta E_{0} = 0$ and has the weakest large-$m$ decrease to negative values for 2-ML-Ag/NiAl (and for 4-ML slabs) versus 1-ML- and 3-ML-Ag/NiAl. The extent of increase reflects the strength of both linear trio attractions and of second NN pair and bent trio repulsions. Thus, the transformation to 2D islands is most difficult in the first two cases.

The above analysis shows explicitly energetics of the 1D to 2D transformation pathway only for a special subset of configurations; however, there is some evidence from simulations that these configurations are relevant for the transition to 2D islands. Thus, the above behavior might reflect the minimum energy path through the complex configuration space but likely also reflects trends in energetics for more complex pathways. Note also that relative to the above quasi-equilibrium analysis, evolution from 1D chains to 2D islands is

**Figure 4.** (a) Schematic for shifting $n(n-1)$ adatoms from a chain end to the side creating an $n \times n$ square. (b) Energy cost $\Delta E_{m}$ versus $n$ comparing Au on 1-, 2-, and 3-ML Ag(100) on Al-terminated NiAl(100).
enhanced by deposition, which creates a supersaturation of adatoms on chain sides. This feature should facilitate the formation of new rows in 2D structures.

In summary, unusually strong linear trio attractions are shown to drive the formation of single-atom wide Au chains on bulk Ag(100) and also on certain Ag(100) thin films sometimes enhanced by QSE. This behavior is demonstrated by KMC simulations of a predictive atomistic model with ab initio kinetics; however, deeper understanding of this behavior follows from a targeted analysis of kinetics of key edge diffusion and 1D-to-2D NC transformation processes. For Au deposited on bulk Ag(100), side-to-end rounding is effectively irreversible, naturally inducing chain formation. For Au deposited on thin Ag(100) films, modified energetics due to QSE impact chain formation. Often end-to-side rounding is facile, so chain formation and survival here is more subtle, reflecting an effective barrier for transformation from 1D to 2D structures.

■ ASSOCIATED CONTENT

+ Supporting Information
Details of our DFT calculations and KMC simulation algorithm. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00636.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES