SUPPLEMENTAL MATERIAL for

Reshaping and sintering of 3D fcc metal nanoclusters: Stochastic atomistic modeling with realistic surface diffusion kinetics

King C. Lai and James W. Evans

Department of Physics & Astronomy and Division of Chemical & Biological Sciences, Ames Laboratory – USDOE, Iowa State University, Ames, Iowa 50011

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S1. Realistic fcc surface diffusion kinetics vs traditional IVA prescriptions

Accurate description of surface diffusion kinetics, including both terrace and step edge diffusion, is necessary for realistic and predictive modeling of 3D nanocluster (NC) evolution. Furthermore, the formulation must simultaneously provide an accurate description of behavior on both {100} and {111} facets, noting that these are most prominent on fcc NCs. Our formulation used for simulation of surface-diffusion mediated 3D NC evolution is crafted to incorporate the flexibility to include desired values for both terrace diffusion and edge diffusion barriers (via appropriate selection of $c_{100TD}$, $c_{111TD}$, $c_{111A}$, and $c_{111B}$). These values may be obtained from appropriate assessment of experimental data or directly from ab-initio Density Functional Theory (DFT) analysis.

In contrast, previous modeling of surface-diffusion mediated shape evolution of 3D fcc NCs has been based on the generic bond-counting or Initial Value Approximation (IVA) formulation [1,2] which does not include this flexibility. In fact, we clarify here that IVA imposes extremely unrealistic values for barriers for these key diffusion processes [3]. It is natural to write the IVA surface atom hop rates in the Arrhenius form, $h = \nu \exp[-E_{act}/(k_B T)]$, where the activation barrier is now selected as $E_{act} = E_0 - E_i$ and where again $E_i$ denotes the total interaction energy for the atom at the initial site before hopping. In a model with just nearest-neighbor (NN) interactions, one has that $E_i = -n_i \phi$, where $n_i$ denotes the initial coordination number $n_i$ for this hopping surface atom. Thus, IVA includes an adjustable free parameter, $E_0$.

For modeling of processes on a specific low-index extended surfaces, $E_0$ is typically chosen to ensure that IVA recovers the terrace diffusion barrier for that low-index surface [3,4]. However, a different choice is required for each different low-index surface, so it is not possible to correctly describe simultaneously terrace diffusion on different facets of 3D nanoclusters. Consider the case of Ag selecting a NN interaction strength $\phi = 0.225$ eV [3]. First, consider modeling targeting Ag diffusion on Ag(100) surfaces. If one wants to recover a reasonable terrace diffusion barrier of say $E_d(100) = 0.425$ eV [3,5], then since $E_d(100) = E_0 + 4\phi$, one must select $E_0 = -0.475$ eV. Consequently, this formulation of IVA imposes a diffusion barrier on {111} facets of $E_d(111) = E_0 + 3\phi = 0.20$ eV which is double the true barrier of $E_d(111) = 0.1$ eV [3,6]!
Even ignoring this serious failure of IVA to simultaneously describe terrace diffusion on different facets, there are additional major shortcomings in the description of key edge diffusion barriers. For example, there is a dramatic failure to describe step edge diffusion on Ag\{100\} surfaces even choosing \(E_0\) to recover terrace diffusion on a Ag\{100\} facet! Specifically, the edge diffusion barrier along close packed steps satisfies \(E_e(100) = E_0 + 5\phi = 0.650 \text{ eV}\) (i.e., 53\% higher than the terrace diffusion barrier) with the above choice of \(E_0 = -0.475 \text{ eV}\). However, a reasonable estimate of the actual barrier is given by \(E_e = 0.275 \text{ eV}\) (i.e., 35\% lower than the terrace diffusion barrier) \([3,7,8]\). Thus, these edge diffusion hopping rates predicted by this version of IVA are typically orders of magnitude lower than actual rates.

Second, for modeling targeting Ag diffusion on Ag\{111\} surfaces. Since \(E_d(111) = E_0 + 3\phi\), one must now choose \(E_0 = -0.575 \text{ eV}\) to recover a reasonable value of \(E_d(111) = 0.10 \text{ eV}\) \([3,6]\). It follows that this IVA prescription enforces \(E_d(100) = E_0 + 4\phi = 0.325 \text{ eV}\) substantially below the more realistic value of \(E_d(100) = 0.425 \text{ eV}\) noted above. Even if we just consider diffusion on Ag\{111\} surface within this IVA formulation, there are still significant shortcomings in the description of step edge diffusion. One has that \(E_e(111) = E_0 + 5\phi = 0.550 \text{ eV}\) which is the same for A- and B-type steps, and is well above the realistic and distinct estimates of \(E_e(111)|_A = 0.275 \text{ eV}\) and \(E_e(111)|_B = 0.300 \text{ eV}\) for the two different types of step edges \([9]\).

The complete failure of IVA kinetics (and the success of our treatment) to realistically describe observations from multiple diverse STM experiments of 2D epitaxial Ag nanoclusters on low-index \{100\} and \{111\} Ag surfaces is illustrated by simulation results and additional analysis presented in the next subsection. Another clear and serious shortcoming of the IVA formulation regarding reshaping of 3D nanoclusters is that the formulation does not and cannot include any Ehrlich-Schwoebel (ES) barriers. However, these additional barriers are important in controlling the rate of mass flow between layers and facets \([3]\).

**S2. 2D epitaxial Ag island formation: Predictions from IVA vs realistic kinetics**

First, we consider the development of non-equilibrium nanocluster growth shapes during Ag deposition on an Ag\{111\} surface with a flux of \(F = 0.003-0.004\) monolayers (ML) per sec. at different temperatures \([9]\). In Fig. S1, we compare experimental STM observations of nanocluster shapes with predictions from our modeling with realistic kinetics and from IVA type modeling (with \(E_0\) tuned to recover the Ag terrace diffusion barrier for this \{111\} surface). Our model reasonably recovers not just the nanocluster density on the surface, but also the non-trivial nanocluster growth shapes. (Successful recovery of the density is a result of matching the experimental terrace diffusion barrier, and also the effective NN interaction strength which determines the extent of reversibility in nanocluster formation \([3]\).) The actual shapes correspond to compact but irregular clusters at 165 K, and more geometric distorted hexagons at 200 K. In contrast, IVA predicts fully developed fractals at both temperatures with the fractals being somewhat denser at the higher temperature. Development of fractal structure is related to the overestimation of IVA of the edge diffusion barrier and thus underestimation of edge diffusion rates (where the denser fractals at higher T reflects the more facile but still strongly inhibited edge diffusion). Since this IVA analysis is tuned to recover the appropriate terrace diffusion barrier and since it uses the same NN interaction strength as simulations using our model, it naturally also recovers the correct nanocluster density.
Second, we consider the development of nanocluster growth shapes during Ag deposition on an Ag\{100\} surface with a flux of $F = 0.006$ monolayers (ML) per sec. at different temperatures [5]. In Fig. S2, we compare experimental STM observations of nanocluster shapes with predictions from our modeling with realistic kinetics and from IVA type modeling (now with $E_0$ tuned to recover the Ag terrace diffusion barrier for this \{100\} surface). Our model again reasonably recovers the nanocluster density on the surface, primarily as a result of matching
the experimental terrace diffusion barrier (noting that nanocluster formation is effectively irreversible in the temperature range considered). In addition, our modeling recovers the observed near square nanoclusters shapes at 250 K and 300 K. In fact, our model also near-square shapes down to 200 K as observed in experiment (not shown). In contrast, IVA predicts fractal nanocluster shapes at 250 K, and compact shapes which are irregular at 300 K (in contrast to the actual near-square shapes). This discrepancy again reflects the overestimation in IVA of step edge diffusion barriers.

**FIG. S2.** Comparison of STM images [5] and model predictions of Ag island growth shapes on Ag(100) with $F = 0.006$ ML/s. The coverage is about 0.1 ML. (a-c) 300 K; (d-f) 250 K. Square simulation cell size 30 x 30 nm$^2$. Experimental image size 25 x 25 nm$^2$ and copyright American Physical Society 2002.

**S3. FCC nanocluster thermodynamics**

Our description of the energetics of various NC configurations uses a lattice-gas modeling with nearest-neighbor (NN) pairwise interactions of effective strength, $\phi$. Specifically, this prescription of energetics is used to evaluate differences, $E_f - E_i$, between energies of initial and final configurations before and after atom hopping.

Support for the effectiveness of this simple prescription of energetics in describing behavior for various fcc metal NC systems comes from a recent DFT analysis and
characterization of such energetics [10]. The key idea in this paper is that the total energy of the NC can be decomposed into a sum of energies for the individual atoms, $E_n$, where these energies depend solely on the coordination, $n$, of the atom. These coordination-dependent single atom energies are determined in a systematic fashion from DFT calculations considering mainly atoms at surfaces with different local configurations and coordination numbers. The key result is that $E_n$ varies nearly linearly with $n$, i.e., $E_n \approx a - bn$ (with $b > 0$), over the considered coordination range, $n \geq 3$. This near-linear variation was observed various metals.

Given this behavior, it is clear that determination of $E_f - E_i$ with this reasonably sophisticated DFT-based description of energetics can be recovered by a model with NN pairwise interactions if one simply chooses $\phi = 2b$. (Here we note that an atom with coordination $n$ is regarded as having $n$ shared bonds of strength with other atoms, so the energy of half of each of these bonds is associated with the atom.) Such an analysis indicates that the effective $\phi \approx 0.20, 0.28, 0.38, 0.40, \text{and } 0.64 \text{ eV for Ag, Cu, Ni, Pt, and Ir, respectively.}$

For Au, $E_n$ versus $n$ deviates more from linearity with higher (lower) values of the effective $\phi$ for smaller (larger) $n$, and we select $\phi = 0.22 \text{ eV}$. We argue that these values reflects the NC surface rather than bulk thermodynamics.

This feature is supported by extracting effective $\phi$ from DFT values of $\{111\}$ and $\{100\}$ surface energies using $\gamma_{111} = \sqrt{3} \phi / a^2$ and $\gamma_{100} = 2 \phi / a^2$ for the NN interaction model. Here, ‘$a$’ denotes the surface lattice constant. From results of DFT analysis for $\gamma_{111}$ using the PBE functional, one obtains $\phi = 0.23, 0.31, 0.43, 0.41, \text{and } 0.61 \text{ eV for Ag, Cu, Ni, Pt, and Ir, respectively.}$ For Au, one obtains $\phi = 0.22 \text{ eV}$. Quite similar values are obtained using DFT values for $\gamma_{100}$, e.g., with $\phi = 0.21 \text{ eV for Ag, and } \phi = 0.23 \text{ eV for Au.}$

Finally, we note that if $E_c$ denotes the bulk cohesive energy, then the above values for effective $\phi$ are far from the choice $\phi(\text{bulk}) = E_c / 6$ which would recover the bulk thermodynamics. Specifically, one has that $\phi(\text{bulk}) = 0.49, 0.58, 0.74, 0.97, \text{ and } 1.16 \text{ eV for Ag, Cu, Ni, Pt, and Ir, respectively, and } \phi(\text{bulk}) = 0.64 \text{ eV for Au.}$

**S4. Comparison of NC sintering for aligned $\{100\}$ versus $\{111\}$ facets**

A schematic of the basic features of the geometry during evolution for aligned $\{100\}$ facets is shown below in Fig. S3a. The stage where a convex shape is first reached corresponds to an eight-sided nanorod where the sides alternate between $\{100\}$ and $\{110\}$ facets. Subsequent evolution requires nucleation of new layers on the $\{100\}$ sides. In contrast, for aligned $\{111\}$ facets, no $\{100\}$ side facets (or $\{111\}$ side facets) are formed in the intermediate stage of evolution. See Fig. S3b. Thus, no nucleation upon such facets is required subsequently.

We also provide further details on simulations described in the text of the sintering of Ag NCs with aligned $\{111\}$ facets. Fig. S4 shows the simulated evolution for two NCs with $N_W = 586$, and $N = 2N_W = 1172$, at 600 K. Fig. S5 shows the evolution of the neck area, $A$ (averaging over 400 trials). In contrast to aligned $\{100\}$ facets, no transition is evident for any $T$ to a necklation-mediated regime. An Arrhenius analysis for the neck filling regime defining a filling time, $\tau_{\text{fill}}$, to correspond to the point where $A/A_{\infty} = 0.6$ (differing from the criterion used of $A/A_{\infty} = 0.45$ for aligned $\{100\}$ facets since the initial neck area is larger for $\{111\}$ aligned facets). The resulting $E_{\text{eff}} \approx 0.70 \text{ eV}$ is slightly lower than those for sintering with aligned $\{100\}$ facets.
FIG. S3. Schematic of geometric evolution during sintering of NCs with: (a) aligned \{100\} facets; (b) aligned \{111\} facets.

FIG. S4. Sintering Ag Wulff NC pair with aligned \{111\} facets for $N_W = 586$ and $N = 2N_W = 1172$ at 600 K.

FIG. S5. Evolution of the scaled neck area for sintering of Ag NCs with aligned \{111\} facets for $N = 1172$ and various temperatures averaging over 400 trials.
S5. Sintering of Au nanoclusters: Modeling versus HRTEM imaging

We describe in more detail our simulations of the sintering of ~4nm Au NCs which are compared with HRTEM observations [12] shown in Fig.4b. Au parameters are selected as $c_{TD100} = 0.60$ eV, $c_{TD111} = 0.125$ eV, $c_{111A} = 0.35$ eV, $c_{111B} = 0.40$ eV, $\delta = 0.12$ eV, and $\phi = 0.22$ eV. The estimates of terrace diffusion barriers can be obtained from the DFT analysis in Ref.[13]. Our assignment of step edge barriers is based in part on the observation that in general for fcc metals, step edge barriers on {100} facets are about 60% of terrace diffusion barriers, and step edge barriers on {111} facets are about 300% of terrace diffusion barriers [14]. In addition, we have performed preliminary DFT analysis to confirm that our choices of barriers are reasonable. The choice of $\delta$ is guided by results for semi-empirical EMT energetics [15], as well as additional studies which model dynamics on Au(111) surfaces [16]. Choice of $\phi$. See Sec. S3.

We choose an individual NC size of $N_W = 2406$ so that the diameter roughly matches that in experiment. The NCs have orientationally aligned {111} facets, but these are slightly offset laterally to better mimic the experimental geometry. We have shown that the offset somewhat increases the initial rate of neck growth, not surprisingly since this makes the neck region a stronger sink for capturing atoms diffusion from the ends on the NC pair. We extract the time scale, $\tau_{\text{fill}} = \tau_{0.6}$ where $A/A_\infty = 0.6$, for the NC pair to evolve to a convex shape. A key goal is to recover the experimentally observed time scale of 128 s without arbitrary adjustment of a prefactor to match experiment as done for IVA based modeling.

Simulations for evolution at 600 K are shown in Fig. S6. We assess neck area growth in a temperature range from 600 K to 750 K as shown in Fig. S7, and obtain characteristic times for filling, $\tau_{\text{fill}} = \tau_{0.6}$ where $A/A_\infty = 0.6$, satisfying $v\tau_{\text{fill}} = 0.23 \times 10^8$, $1.43 \times 10^8$, $4.46 \times 10^8$ at 750 K, 650 K, and 600 K, respectively. A corresponding Arrhenius analysis presented in Fig. S8 yields $E_{\text{eff}} = 0.77$ eV. This enables reliable extrapolation of values of $\tau_{\text{fill}}$ values to lower temperature to obtain $\tau_{\text{fill}} \approx 130$ s at 300 K choosing $v = 10^{13}$/s.

![Image](image_url)

**FIG. S6.** Evolution of the scaled neck area for sintering of Au NCs with aligned but laterally offset {111} facets and $N = 2N_W = 4812$ at 600 K.
**FIG. S7.** Evolution of the scaled neck area for sintering of Au NCs with aligned but laterally offset \{111\} facets for \(N = 4812\) and various temperatures averaging over 65 trials.

**FIG. S8.** Arrhenius behavior for neck-filling for sintering on Au NCs with aligned but laterally offset \{111\} facets for \(N = 4812\).

**S6. Pinch-off of Ag nanorods.**

Synthesized octagonal Ag nanorods have alternating \{100\} and \{110\} side facets, and \{100\} end facets [1]. Experiments [17], continuum theory [18], and atomistic simulation (which did not satisfy detailed-balance [19]) suggest the existence of a Rayleigh-Plateau type pinch-off instability above critical aspect ratio, \(R_c\). Continuum theory for isotropic surface energy and diffusion indicates an instability with wavelength \(\lambda \approx 4.45 \times \text{rod diameter} [19]\), so 4.5 gives rough estimate of \(R_c\). Simulations illustrated Fig. S9 suggest that \(R_c \approx 7-8\) for the selected rod width, the difference in \(R_c\) reflecting faceting and nanoscale effects.
Fig. S9. Pinch-off of octagonal Ag nanorod with $N = 2202$, $T = 700K$.

References