SECTION 1. Definition of Surface and Bulk Free Energy

The face- and concentration-dependent surface free energy, defined as the excess energy per unit area due to the presence of a surface, must include a term correcting for the composition difference between bulk and surface, i.e.

$$\gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)} = \gamma_{(n,C_1^S,C_2^S,\dots)} + \tau\left(G_{(C_1^S,C_2^S,\dots)} - G_{(C_1^V,C_2^V,\dots)}\right) \tag{1}$$

Where τ is the surface thickness, $\gamma_{(n,C_1^S,C_2^S,\dots)}$ is the free energy of a surface of crystallographic orientation n and concentration $C_1^S, C_2^S, \dots$ on a bulk of the same concentration, and $\gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)}$ is the free energy of a surface of concentration $C_1^S, C_2^S, \dots$ on a bulk of concentration $C_1^V, C_2^V, \dots$. The bulk free energy, G, is defined as the deviation from a linear variation of bulk free energy between two pure compounds.

Expanding this term via a truncated Taylor expansion for a small change in surface composition x_i^S yields

$$\gamma_{(n,C_1^S+x_1^S,C_1^V,C_2^S+x_2^S,C_2^V,\dots)} = \gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)} + \sum \frac{d\gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)}}{d(C_i^S)}(x_i^S) \tag{2}$$

The surface chemical potential is defined as the derivative of the free energy with respect to concentration,

$$\mu_i^S = \frac{d\gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)}}{d(C_i^S)} \tag{3}$$

Thus

$$\gamma_{(n,C_1^S+x_1^S,C_1^V,C_2^S+x_2^S,C_2^V,\dots)} = \gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)} + \sum \mu_i^S\left(x_i^S\right) \tag{4}$$

The total surface energy of the particle, E^S, is the sum of surface free energies over the entire particle,

$$E^S = \int\left(\gamma_{(n,C_1^S,C_1^V,C_2^S,C_2^V,\dots)} + \sum \mu_i^S\left(x_i^S\right)\right) dS \tag{5}$$

Analogously, the bulk free energy can be expressed as a Taylor series for a small change in bulk composition x_i^V,

$$G_{(C_1^V+x_1^V,C_2^V+x_2^V,\dots)} - G_{(B_1^V,B_2^V,\dots)} = G_{(C_1^V,C_2^V,\dots)} - G_{(B_1^V,B_2^V,\dots)} + \sum \frac{dG_{(C_1^V,C_2^V,\dots)}}{d(C_i^V)}(x_i^V) \tag{6}$$

Where the B_i^V terms refer to the initial concentration assuming equal bulk and surface composition; we refer to this as the homogeneous concentration.

The bulk chemical potential is defined as

$$\mu_i^V = \frac{dG^V{}_{(Cv1,Cv2..)}}{dC_i^V} \tag{7}$$

Thus

$$G_{(C_1^V + x_1^V, C_2^V + x_2^V, ...)} - G_{(B_1^V, B_2^V, ...)} = G_{(C_1^V, C_2^V, ...)} - G_{(B_1^V, B_2^V, ...)} + \sum \mu_i^V (x_i^V) \tag{8}$$

The change in bulk energy, E^V, is expressed as

$$E^V = \int (\Delta G + \sum \mu_i^V (x_i^V)) \, dV \tag{9}$$

Where the bulk free energy term ΔG is the difference between the free energy of the final bulk concentration $C_1^V, C_2^V, ...$ and that of the initial composition $B_1^V, B_2^V, ...,$

$$\Delta G = G_{(C_1^V, C_2^V, ...)} - G_{(B_1^V, B_2^V, ...)} \tag{10}$$

SECTION 2. Derivation of Wulff Construction for Alloy Particles

We first apply a conservation of mass constraint,

$$F_i = \int \tau [(C_i^S + x_i^S) - (C_i^V + x_i^V)]dS + \int (C_i^V + x_i^V)dV \tag{11}$$

And a constant volume constraint,

$$F_V = \int dV \tag{12}$$

The global problem can thus be written as minimizing via the Lagrangian multipliers Λ and λ_i,

$$F = E^S + E^V - \Lambda(F_V - A) - \sum \lambda_i(F_i - B_i) \tag{13}$$

Where A and B_i are constants.

Composition conservation requires that

$$\frac{dF}{d\lambda_i} = 0$$

Such that

$$0 = (F_i - B_i) \tag{14}$$

Equation 13 thus becomes

$$F = E^S + E^V - \Lambda(F_V - A) \tag{15}$$

Combining Equations. 5, 9, and 15 and rearranging yields

$$F = \int [\gamma_{(n,c_1^S,c_1^V,c_2^S,c_2^V,\dots)} + \sum \mu_i^S (x_i^S)]dS + \int [\Delta G + \sum \mu_i^V (x_i^V) - \Lambda]dV + \Lambda A \tag{16}$$

The derivative of the energy with respect to a change in composition, in the bulk or the surface, must be zero at equilibrium, i.e.

$$\frac{dF}{dx_i^S} = \frac{dF}{dx_i^V} = 0 \tag{16}$$

This greatly simplifies Equation 16, which becomes

$$F = \int \gamma_{(n,c_1^S,c_1^V,c_2^S,c_2^V,\dots)} dS + \int (\Delta G - \Lambda)dV + \Lambda A \tag{17}$$

Noting that the conventional Wulff problem (without alloying) is minimizing

$$F = E^S - \Lambda_c F_V \tag{18}$$

3

i.e.

$$F = \int \gamma_{(n)} dS - \int \Lambda_c dV \tag{19}$$

with a solution

$$\gamma = \Lambda_c h \tag{20}$$

We immediately obtain the solution of Equation 17,

$$\gamma_{(n, c_1^S, c_1^V, c_2^S, c_2^V, ...)} = h_{(n)}\{\Lambda - \Delta G\} \tag{21}$$

Rearranging gives the alloy nanoparticle Wulff construction

$$\frac{\gamma_{(n, c_1^S, c_1^V, c_2^S, c_2^V, ...)}}{\{\Lambda - \Delta G\}} = h_{(n)} \tag{22}$$

Which dictates the face-dependent equilibrium surface normal $h_{(n)}$, i.e. the particle shape, as a function of surface composition, bulk composition, and particle size.

Neglecting change in bulk concentration due to surface segregation, i.e. setting ΔG=0 leads as expected to a form analogous to the traditional Wulff construction,

$$\frac{\gamma_{(n, c_1^S, c_1^V, c_2^S, c_2^V, ...)}}{\Lambda} = h_{(n)} \tag{23}$$

The thermodynamic equilibrium energy is then simply the sum of surface free energy and change in bulk energy,

$$E_{tot} = E^S + E^V = \int \gamma_{(n, c_1^S, c_2^S, ...)} dS + \int \Delta G \, dV \tag{24}$$

SECTION 3. Details on Free Energy and Unit Cell Parameter Values Used

The free energy and unit cell parameters used are defined below and summarized in Table S1.

Bulk Free Energy
Bulk free energy from literature values (experimental when available, calculations otherwise) was fit by a polynomial.
For CuAu, AuPd, and AgAu:
$$G = B * [Au]^3 + C * [Au]^2 + D * [Au] \tag{25}$$
For AgPd:
$$G = A * [Pd]^4 + B * [Pd]^3 + C * [Pd]^2 + D * [Pd] \tag{26}$$

Unit Cell Parameter (c)
The unit cell parameter was assumed to vary linearly between that of pure components. Experimental values were used.
For CuAu, AuPd, and AgAu:
$$c = E * [Au] + F \tag{27}$$
For AgPd:
$$c = E * [Pd] + F \tag{28}$$

Homogeneous Surface Free Energy
Surface free energy from literature values (experimental when available, calculations otherwise) were assumed to vary linearly between pure components.
For CuAu, AuPd, and AgAu:
$$\gamma_{(n,c_1^S,c_2^S,\ldots)} = \alpha_{(n)} * [Au] + \beta_{(n)} \tag{29}$$
For AgPd:
$$\gamma_{(n,c_1^S,c_2^S,\ldots)} = \alpha_{(n)} * [Pd] + \beta_{(n)} \tag{30}$$

TABLE S.I Parameters used for the computation of the bulk free energy (A-D, Equations 25-26), the unit cell parameter (E-F, Equations 27-28) and the surface free energy (α-β, Equations 29-30) of CuAu, AuPd, AgAu and AgPd [1-8]. The concentration used are unitless fractions, thus the coefficients do not contain concentration units.

	T (K)	A (10^9 J/m^3)	B (10^9 J/m^3)	C (10^9 J/m^3)	D (10^9 J/m^3)	E (10^{-10} m)	F (10^{-10} m)	$\alpha_{(100)}$ (J/m^2)	$\beta_{(100)}$ (J/m^2)	$\alpha_{(111)}$ (J/m^2)	$\beta_{(111)}$ (J/m^2)
CuAu	720	-	-2.293	5.7414	-3.4458	0.4645	3.663	-0.2946	1.184	-0.3657	1.067
AuPd	600	-	0	1.667	-16.67	0.2083	3.907	-0.1260	1.001	-0.1931	0.8870
AgAu	600	-	0	0.9686	-0.9705	0.01070	4.104	0.2310	0.6490	0.0600	0.6339
AgPd	915	3.194	-6.957	6.253	-2.480	-0.2089	4.133	0.3390	0.6164	0.2404	0.6020

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SECTION 4. MATLAB Code Overview

The MATLAB code used calculated the value of Λ, h_{100}, h_{111}, bulk concentration, surface concentration, and total energy for a given range of initial (homogeneous) composition, cycling through each initial composition and each possible surface composition. The inputs were the number of atoms, an initial guess on Λ, the range and step size desired for the surface and initial concentration, as well as the parameters (Table S1) and functions describing the surface free energy (Equations 29-30), the bulk free energy (Equations 25-26), and the unit cell change with composition (Equations 27-28).

Since the surface concentration is fixed in each loop, the bulk concentration can be calculated by knowing the shape, i.e. the number of surface atoms. In the code, the first approximation for Λ (after the initial guess input), h_{111}, and h_{100}, was calculated by solving the basic Wulff model (Equation 23). Then the Λ in the alloy Wulff model was solved for twice and all concentrations and shape parameters were recalculated at each step. It was found that this number of repetition was sufficient to reach convergence. Concentrations above unity or below zero were set to unity and zero, respectively, and parameters were calculated with the fixed parameters.
The lowest energy configuration was then found from the energy matrix output in the previous step. Similarly, h_{111}/h_{100} ratios could be calculated from the output h_{111} and h_{100} matrices from knowing the lowest energy configuration.

All MATLAB codes used are available upon request.
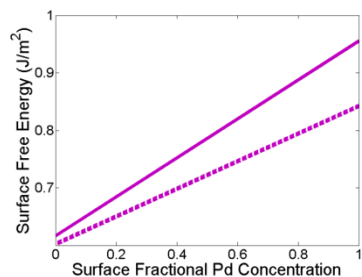
SECTION 5. Results for AgPd

Figure S. 1. Surface free energy for the 100 (solid line) and 111 (dashed line) faces of AgPd.
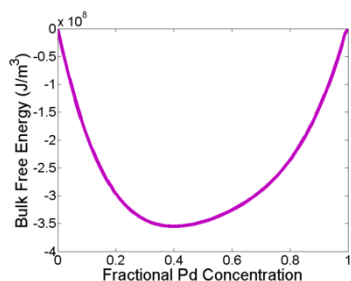

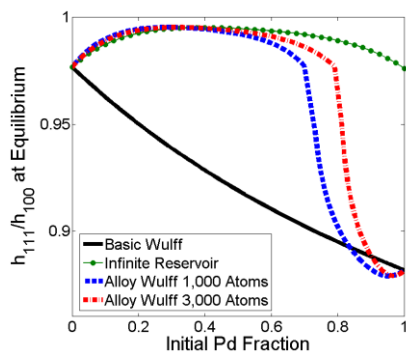Figure S. 2. Bulk free energy for the random FCC alloy AgPd.

Figure S. 3. Shape dependence on size and composition according to the alloy Wulff model for AgPd. Size and composition dependence of the particle shape computed for an homogeneous alloy (Basic Wulff, solid black line), a segregating alloy with an infinite reservoir approximation (green line with round markers), and the current Alloy Wulff model (blue dashed line for 1,000 atoms and red dot-dashed line for 3,000 atoms). The behavior of AgPd is comparable to that of AgAu (Figure 2).
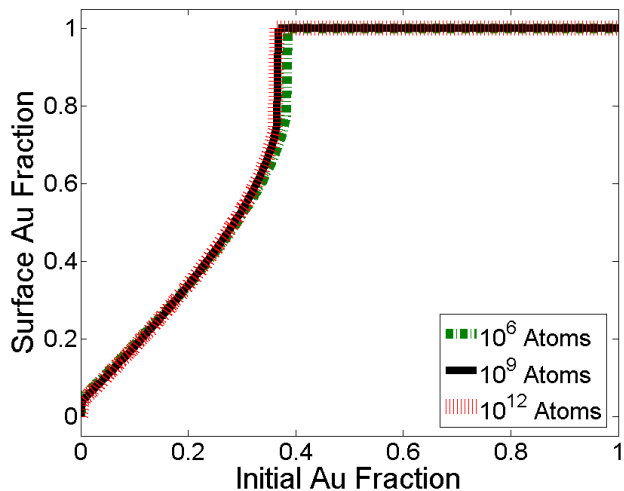
SECTION 6. Additional Figures for CuAu

Figure S. 4. Effect of size and initial (homogeneous) composition on the equilibrium surface composition of large CuAu alloy nanoparticles. Particles containing 10^6, 10^9, 10^{12} atoms (~ 30, 00, and 3000 nm diameter) are represented by green dot-dashed, solid black, and red dotted lines, respectively.
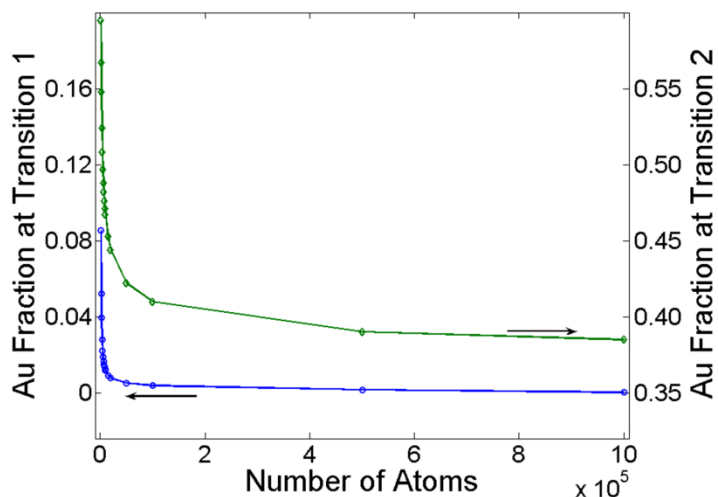

Figure S. 5. Size-dependence of transition 1 (regime 1 to regime 2, blue circles) and transition 2 (regime 2 to regime 3, green diamonds) for the strong alloy CuAu. The arrows point to the appropriate scale.