In-situ Transmission Electron Microscopy Observations of Sublimation in Silver Nanoparticles

Michael A. Asoro[1], Desiderio Kovar[1, 2], Paulo J. Ferreira[1, 2]

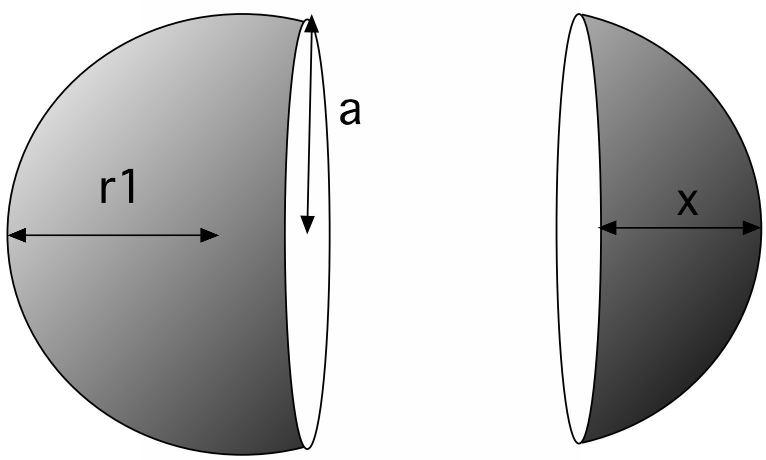
[1]Materials Science and Engineering Program and [2]Department of Mechanical Engineering,

University of Texas at Austin, Austin, TX 78712, USA

Appendix: Derivation of Sublimation Energy for Facetted and Unfacetted Particles

Consider state 1 as a spherical particle of radius r_1. The total energy of the particle, E_1, is given by, $E_1 = \gamma_s (4 \pi r_1^2) + V(G_{vs}) = \gamma_s (4 \pi r_1^2) + (4/3 \pi r_1^3 G_{vs})$, where V = volume of the sphere and G_{vs} is the volume free energy of the solid.

If the particle facets by splitting into two {111} facetted particles of size x and $2r_1$ - x as shown below, the total energy is given by $E_2 = \gamma_s(4\pi r_1^2) + 2\gamma_{s111}A_{111} + (4/3\, \pi\, r_1^3\, G_{vs})$



To determine A_{111}, we note that the radius of the white circular facetted region, a, = $[(2r_1x)-x^2]^{1/2}$. Thus, $E_2 = \gamma_s(4\pi r_1^2) + 2\pi\gamma_{s111}\, [(2r_1x) - x^2] + (4/3\, \pi\, r_1^3\, G_{vs})$.

Then, if the smaller facetted particle on the right subsequently sublimates, then the total energy of the system = E_3 = surface energy of larger facetted particle + volume energy of larger facetted particle + volume energy of smaller facetted particle (which now consists of vapor and therefore has no interfacial area).

The surface area of the smaller particle is $2 \pi r_1 x$, not counting the white facetted portion, and the volume of the smaller particle is $1/6\, \pi\, x\, (3a^2 + x^2) = (\pi)\, (r_1 x^2 - x^3/3)$

$E_3 = \{[\gamma_s[(4\pi r_1^2) - 2\, \pi\, r_1 x] + \pi\gamma_{s111}\, [(2r_1x) - x^2]\} + \{G_{vs}\, [(4/3\, \pi\, r_1^3) - (\pi)(r_1 x^2 - x^3/3)]\} + \{G_{vv}\, [(\pi)(r_1 x^2 - x^3/3)]]\}$, where G_{vv} is the volume free energy of the vapor.

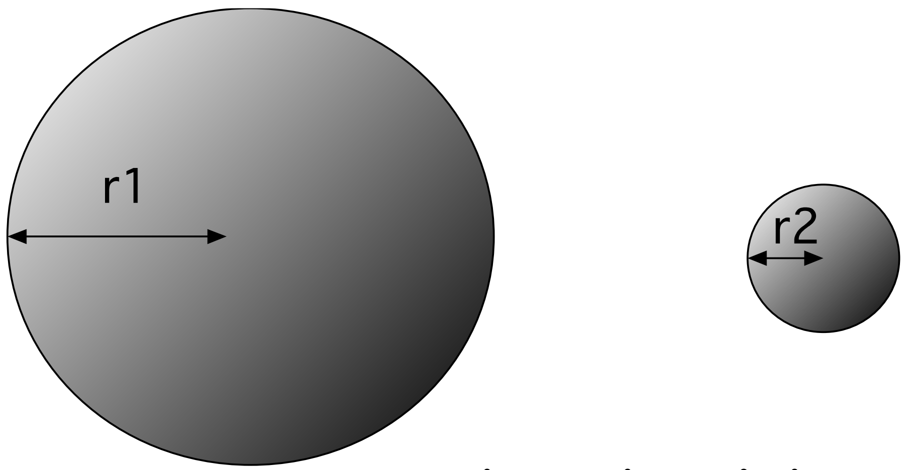
The change in energy on going from state 1 → 3 is $\Delta E_f = E_3 - E_1$. Thus,

$\Delta E_f = \pi\gamma_{s111}\, (2r_1x - x^2) - 2\, \pi\gamma_s\, r1\, x + (G_{vv} - G_{vs})(\pi\, r1\, x^2) - (G_{vv} - G_{vs})\, \pi\, x^3/3$

If $E_{sub} \overset{\text{def}}{=} G_{vs} - G_{vv}$, then

$\Delta E_f = \pi\gamma_{s111}\,(2r_1 x - x^2)$-2 $\pi\gamma_s$ r1 x + $E_{sub}\left(\frac{\pi x^3}{3} - \pi\, r1\, x^2\right)$

The relevant comparison is to compare ΔE_f above to the energy change for the uniform sublimation, ΔE_f, for a spherical particle with radius r_1 to a smaller spherical particle r_2 where the smaller spherical particle has the same volume as the larger facetted particle above.



To determine r_2, we note that $4/3\,\pi\, r_2^3 = 4/3\,\pi\, r_1^3 - (\pi)(r_1 x^2 - x^3/3) \rightarrow r_2 = [r_1^3 - \tfrac{3}{4} r_1 x^2 - x^3/(4))]^{1/3}$.
The energy change for going from the large to the small particle by uniform sublimation is then given by,
$\Delta E_{nf} = \{\gamma_s (4\,\pi\, r_2^2) + G_{vs}(4/3\,\pi\, r_2^3) + G_{vv}[(4/3\,\pi\, r_2^3 - 4/3\,\pi\, r_1^3)]\} - [\gamma_s(4\,\pi\, r_1^2) + (4/3\,\pi\, r_1^3\, G_{vs})]$

Again, defining $E_{sub} \stackrel{\text{def}}{=} G_{vs} - G_{vv}, \rightarrow$

$\Delta E_{nf} = \{4\,\pi\gamma_s\,(r_2^2 - r_1^2) + 4/3\pi E_{sub}\,(r_2^3 - r_1^3)$ where $r_2 = [r_1^3 - \tfrac{3}{4}(r_1 x^2 - x^3/(4\pi))]^{1/3}$

We use the following values for material properties of Ag, $\gamma_s = 1.2$ J/m^2, $\gamma_{\{111\}} = 0.62$ J/m^2, E_{sub} = 284 KJ/mol = 2.765×10^{10} J/m^3 (this is temperature dependent), and use these to calculate the change in energy for different values of x/r and r.