Thermodynamics and Kinetics of Nanomaterials Synthesis
Okinawa Institute of Science and Technology
Spring 2015

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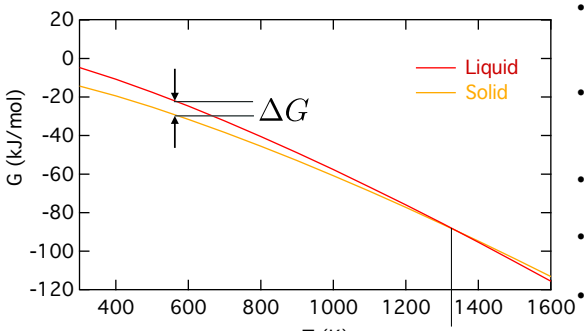
Lecture 5, 3 June 2015

Nanoparticle Nucleation and Growth from the Vapor Phase

- Turnbull Extrapolation to estimate free energy differences
  - Liquid-solid case
  - Vapor-solid case
- Effect of pressure on driving force
- Temperature of atomic species – thermalization
- Pressure of atomic species – flux, velocity and temperature
- Critical nucleus size
- Remarks on nucleation and growth

Driving Force for Solidification



$$\Delta G \equiv G^L - G^S$$

- Free energy of liquid and solid gold as a function of temperature
- Obtained from parameterized free energy expressions fit to experimental data
- Empirical or semi-empirical approach
- Widely used in calculations of phase diagrams
- For example see, FREED Database

At the melting point, there is no driving force for solidification

$$\Delta G(T_M) = 0 = \Delta H(T_M) - T_M \Delta S(T_M)$$

$$\Delta S(T_M) = \frac{\Delta H(T_M)}{T_M}$$

Turnbull Extrapolation

$\Delta G \equiv G^L - G^S$ Driving force for solidification

$= H^L - TS^L - H^S + TS^S$

Using the melting temperature as a reference, we can write:

$$H = H(T_M) + \int_{T_M}^{T} C_P \, dT \quad \text{and} \quad S = S(T_M) + \int_{T_M}^{T} \frac{C_P}{T} \, dT$$

This gives:

$$\Delta G = \Delta H(T_M) - T\Delta S(T_M) + \int_{T_M}^{T} \Delta C_P \, dT - T \int_{T_M}^{T} \frac{\Delta C_P}{T} \, dT$$

Using: $\Delta S(T_M) = \frac{\Delta H(T_M)}{T_M}$

We find for the driving force away from the melting point:

$$\Delta G = \Delta H(T_M) \left(1 - \frac{T}{T_M}\right) + \int_{T_M}^{T} \Delta C_P \, dT - T \int_{T_M}^{T} \frac{\Delta C_P}{T} \, dT$$

Turnbull Extrapolation

$\Delta G \equiv G^L - G^S$ General expression

$$\Delta G = \Delta H(T_M) \left(1 - \frac{T}{T_M}\right) + \int_{T_M}^{T} \Delta C_P \, dT - T \int_{T_M}^{T} \frac{\Delta C_P}{T} \, dT$$

Turnbull assumes the curvatures of the free energies are the same so $\Delta C_P = 0$

Giving: $$\Delta G = \Delta H_F \left(1 - \frac{T}{T_M}\right)$$

Turnbull Extrapolation

- Named after the late David Turnbull
- A giant in field of materials science, kinetics and thermodynamics, particularly the science of nucleation
- Did much of his seminal work while at General Electric laboratories
- Later went to Harvard University
- A kind and supportive mentor, friend and colleague

Turnbull Extrapolation

$$\Delta G \equiv G^L - G^S \qquad \boxed{\Delta G = \Delta H_F \left(1 - \frac{T}{T_M}\right)}$$

Turnbull Extrapolation

Can also be seen to result from a Taylor series expansion of the free energy functions around the melting point

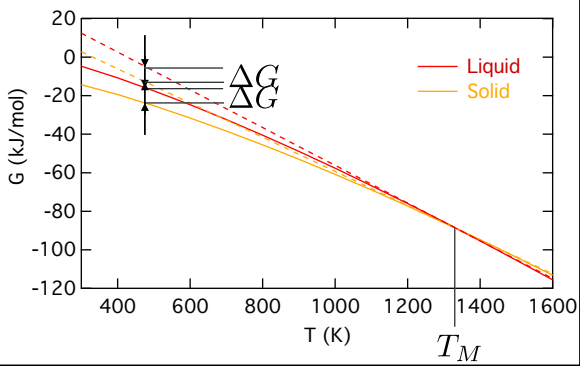
$$G \approx G(T_M) + (T - T_M) \left.\frac{dG}{dT}\right|_{T=T_M}$$

From our thermo treatment:

$$\left.\frac{dG}{dT}\right|_{T=T_M} = -S(T_M)$$

$$\Delta G = G^L(T_M) - G^S(T_M) - \Delta S(T_M)(T - T_M)$$

$$= \Delta H_F \left(1 - \frac{T}{T_M}\right)$$

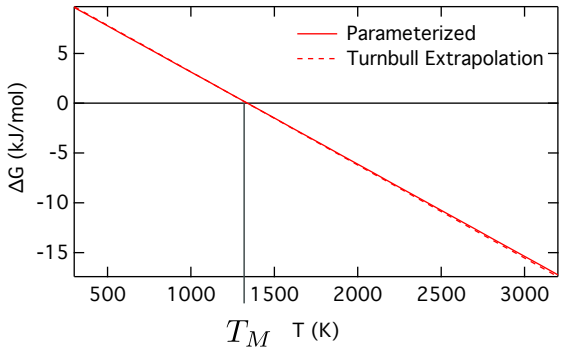


Turnbull Extrapolation

$$\Delta G \equiv G^L - G^S \qquad \boxed{\Delta G = \Delta H_F \left(1 - \frac{T}{T_M}\right)}$$

Turnbull Extrapolation

Driving force for solidification of gold



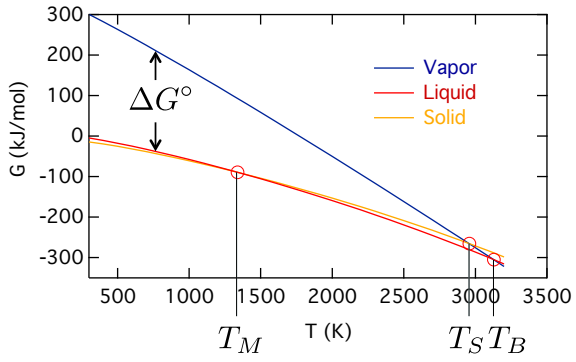
Condensation from the Vapor Phase

We first turn to thermodynamics (of course!)

- How large is the driving force for condensation from the vapor to the solid (or liquid)

$$\Delta G^\circ - G^\circ_{\text{vapor}} - G^\circ_{\text{solid}}$$

- Here we use ° to reflect that this free energy difference is between vapor and solid in their standard states
- Standard state of the solid is its pure form
- Standard state of a vapor is one atmosphere pressure
- Both at the temperature of interest



Driving Force Approximation

A straightforward extension of our Turnbull extrapolation treatment yields:

$$\Delta G^\circ = \Delta H_f \left(1 - \frac{T}{T_M}\right) + \Delta H_v \left(1 - \frac{T}{T_B}\right)$$

Melting temperature

Boiling temperature

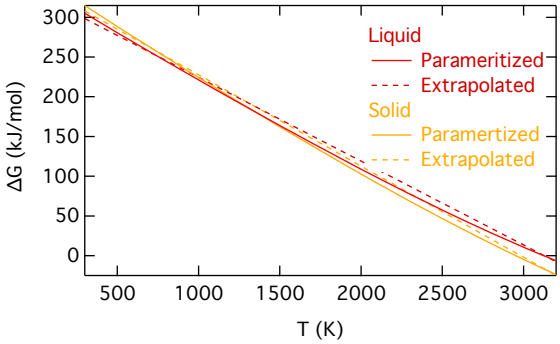
Enthalpy of fusion

Enthalpy of vaporization

How well does this work?

Pretty well.

- For now we ignore the effect of size on the chemical potential, wile recognizing that small particles might actually be liquid rather than solid, and that they might solidify as they grow
- But we aren't done with the driving force yet …



Driving Force: Effect of Pressure

A straightforward extension of our Turnbull extrapolation treatment yields:

$$\Delta G^\circ = \Delta H_f \left(1 - \frac{T}{T_M}\right) + \Delta H_v \left(1 - \frac{T}{T_B}\right)$$

- This driving force is the difference between vapor in its standard state and the solid in its standard state
- The standard state of vapor is one atmosphere
  - Partial pressures of the condensing vapor are likely onsiderably lower than one atmosphere

Assuming ideal gas behavior we have:

$$\Delta G = \Delta G^\circ + RT \ln P$$

By setting $\Delta G = 0$ we find the equilibrium pressure

$$P_{\text{eq}} = e^{-\Delta G^\circ / RT}$$

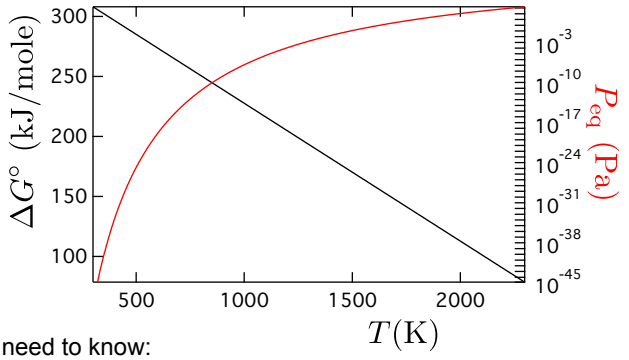
$$\Delta G = RT \ln \left(\frac{P}{P_{\text{eq}}}\right)$$

Driving Force: Effect of Pressure

$$\Delta G^\circ = \Delta H_f \left(1 - \frac{T}{T_M}\right) + \Delta H_v \left(1 - \frac{T}{T_B}\right)$$

$$\Delta G = \Delta G^\circ + RT \ln P \qquad P_{\text{eq}} = e^{-\Delta G^\circ / RT}$$

$$\Delta G = RT \ln \left(\frac{P}{P_{\text{eq}}}\right)$$

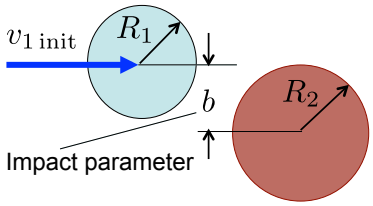


To find the driving force we need to know:

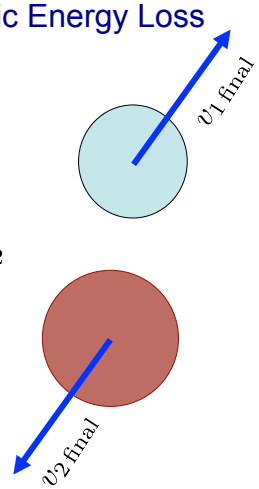
- Temperature
- Pressure of nanoparticle species

Temperature of Nanoparticle Species: Kinetic Energy Loss

- Sputtered species leaves target with high energy (~ 10 eV)
- Experiences collisions with relatively cool inert gas ions
  - Lose kinetic energy with each collision
- We treat collisions as collisions between hard spheres



$$R_0 = R_1 + R_2$$



Ratio of kinetic energy after and before collision

$$\frac{E_{kf}}{E_{ki}} = 1 - \frac{4M_1M_2}{(M_1+M_2)^2}\left[1 - \left(\frac{b}{R_0}\right)^2\right]$$

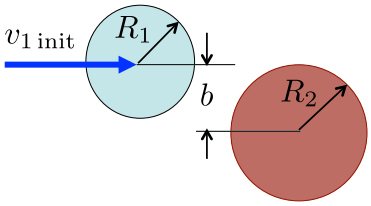
Average over impact parameter with appropriate probability distribution $\mathcal{P}(b) = \dfrac{2b}{R_0}$

$$\left\langle \frac{E_{kf}}{E_{ki}} \right\rangle = \int_0^{R_0} \frac{E_{kf}}{E_{ki}}\,\mathcal{P}(b)\,db = 1 - \frac{2M_1M_2}{(M_1+M_2)^2}$$

Temperature of Nanoparticle Species

- Average Kinetic energy ratio after 1 collision

$$\left\langle \frac{E_{kf}}{E_{ki}} \right\rangle = 1 - \frac{2M_1M_2}{(M_1+M_2)^2} \equiv f$$

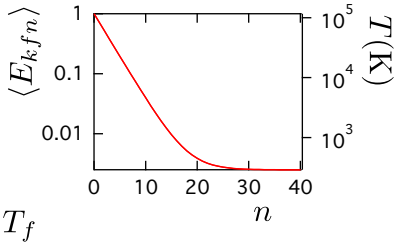


- Kinetic energy after *n* collisions

$$\langle E_{kfn} \rangle = \langle E_{ki} \rangle f^n$$

- Only valid until final kinetic energy approaches thermal energy
  - We add thermal energy
- Gives an idea of how far an energetic species can travel until it is thermalized
- Atoms are essentially thermalized after 20-30 collisions
- More detailed model presented in Bogaerts et al JAP 1995.
- We relate kinetic energy to temperature in the normal fashion

$$T = \frac{E_{kfn}}{k_B} = T_0 f^n + T_f$$



Number of Collisions Per Distance

- Mean free path from the kinetic theory of gasses

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d_c^2 P}$$

Element	Diameter
Ar	0.367 nm
Au	0.35 nm

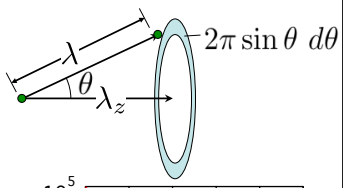
Plugging in numbers we find for T = 300 K:

$$\lambda(\text{mm}) \approx \frac{7.5}{P(\text{Pa})}$$

So for a deposition pressure of *P* ~ 15 Pa (113 mT) we find:

$$\lambda \approx 0.5 \text{ mm}$$

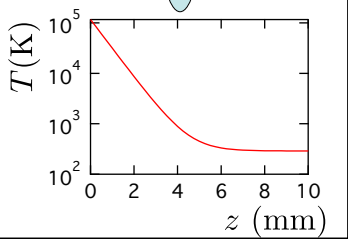
- Relate to distance traveled along the axis of the source (*z* direction)
- Assume that fast atom has same MFP in cold gas as cold gas atom
- Assume that we average over all positive *z* trajectories with equal probability



$$\langle \lambda_z \rangle = \frac{1}{2\pi} \int_0^{\pi/2} \lambda \cos\theta \; 2\pi \sin\theta \; d\theta = \frac{\lambda}{2}$$

$$z = n\langle \lambda_z \rangle = \frac{n\lambda}{2} \qquad n = \frac{2z}{\lambda}$$

- Thus we can find the Au atom "temperature" as a function of distance from the source



Nanocluster Atom Pressure (Density)

Flux of sputtered atoms due to ion current and sputter yield:

Flux of atoms leaving target

$$j_0 = j_I \eta = \frac{\eta I}{eA}$$

Sputter current

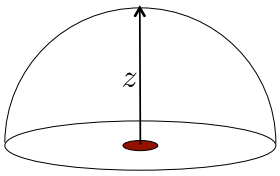
Target area

Sputter yield

Flux of ions hitting target

Conservation of atoms:

$$j_0 A = j(z) 2\pi z^2$$



$$j(z) = \frac{j_0 A}{2\pi z^2}$$

Sputtered atom pressure

$$j = \langle v \rangle \rho = \langle v \rangle \frac{P}{k_B T} \qquad P = \frac{k_B T j}{\langle v \rangle}$$

Nanocluster Atom Pressure (Density)

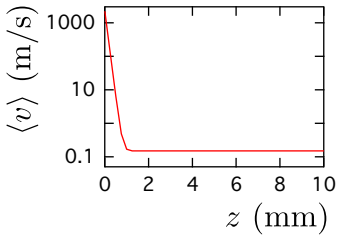
Flux of sputtered atoms due to ion current and sputter yield:

Sputtered atom pressure $P = \dfrac{k_B T j}{\langle v \rangle}$

Sputtered atom drift velocity

- Initially the velocity is high and directed away from the sputter source
- After a few scattering events, the velocity direction becomes randomized
  - Here we assume the outward component of velocity is cut in half due to direction randomization
- Eventually the average velocity becomes just the drift velocity of the process gas

$$\langle v \rangle = \sqrt{\frac{RT}{M}} \left(\frac{1}{2}\right)^{2z/\lambda} + v_{\text{drift}}$$



Nanocluster Atom Pressure (Density)

Flux of sputtered atoms due to ion current and sputter yield:

Sputtered atom pressure $P = \dfrac{k_B T j}{\langle v \rangle}$

Sputtered atom flux $j(z) = \dfrac{j_0 A}{2\pi z^2}$

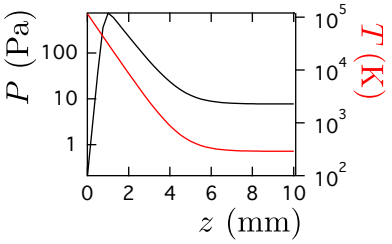
Sputtered atom average velocity $\langle v \rangle = \sqrt{\dfrac{RT}{M}} \left(\dfrac{1}{2}\right)^{2z/\lambda} + v_{\text{drift}}$

Sputtered atom temperature

$$T = \left[1 - \frac{2M_1 M_2}{(M_1 + M_2)^2}\right]^{2z/\lambda} + T_0$$

Numbers used:

$v_{\text{drift}} = 15$ cm/s $\quad I = 300$ mA $\quad \eta = 0.3$



- Pressure of Au atoms is *much* higher than that associated with normal sputter deposition
- This pressure also assumes that no atoms are bound into nanoparticles

Critical Nucleus Size

Recall our expression for a critical radius

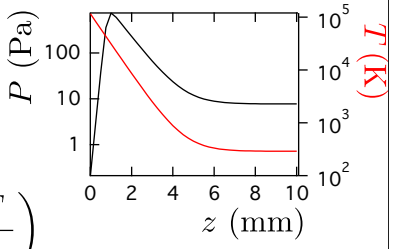
$$r^* = \frac{2\gamma\Omega_s}{\Delta G}$$

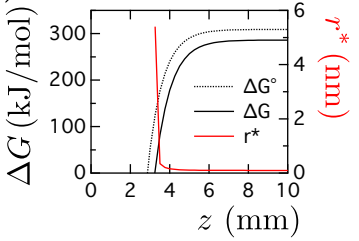
Driving force for precipitation of solid from vapor

$$\Delta G = \Delta G^\circ + RT \ln P$$

Turnbull extrapolation to find standard state value

$$\Delta G^\circ = \Delta H_f \left(1 - \frac{T}{T_M}\right) + \Delta H_v \left(1 - \frac{T}{T_B}\right)$$





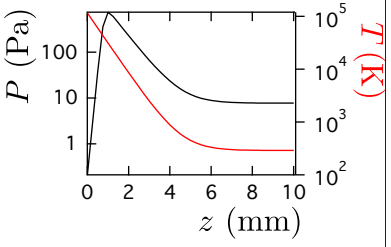
Observations:

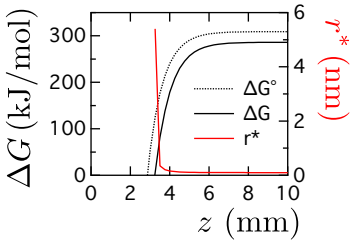
- The driving force is negative until the effective temperature of the sputtered atoms drops due to about 12 collisions with the Ar atoms
- The critical size rapidly drops to atomic scale almost as soon as the driving force becomes positive
- Nucleation will be dominated by atom-atom collisions

$$n = \frac{2z}{\lambda} \qquad \lambda \approx 0.5 \text{ mm}$$

Nucleation and Growth Rate

- Nucleation will occur when two cool atoms collide
- This will reduce the number of free atoms
- Growth will occur when free atoms collide with a nucleus
- This will also reduce the number of free atoms
- Actual pressure of free atoms will drop as a function of z due to removal of atoms from nucleation and growth of nanoparticles





Summary of Formation of Nanoparticles from the Vapor Phase

- We explored the Turnbull extrapolation to estimate free energy difference for liquid-solid case and vapor solid case
  - Good agreement with parameterized free energy expressions
- We included the effect of species pressure on driving force
- We estimated the temperature and pressure of atomic species as a function of distance from the sputter target
  - We found the temperature dropped off quickly with distance relative to the mean free path due to collisions with cool inert gas atoms
  - We found the pressure was much higher than typical in sputter deposition
- We found the critical nucleus size dropped to atomic dimensions very quickly after the driving force became positive
- Remarks on nucleation and growth