NM - nanoparticle synthesis by precipitation methods

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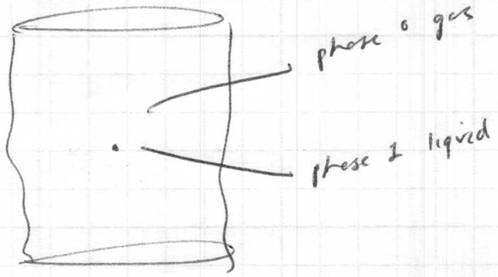
goal: understand mechanisms of nucleation and growth

want to separate these events

nucleation typically requires more energy than growth ; maximize separation by maximizing energy (~ temperature) difference between the 2 steps.

part 1: nucleation of a liquid droplet in a gas atmosphere (volmer-becker capillary approximation ⇒ spherical droplets)



need a nucleation site to grow a particle

upon particle formation, $\Delta G_{tot} = \overbrace{\Delta G_v}^{\text{volume}} + \overbrace{\Delta G_s}^{\text{surface}}$

$$\Delta G_v = \frac{\frac{4}{3}\pi R^3 \underbrace{\Delta\mu}_{\text{change in chemical potential per atom (or molecule) (internal energy change)}}}{\underbrace{a_v}_{\text{atomic volume}}} + \overbrace{4\pi R^2 \gamma}^{\text{surface energy}}$$

$$\Rightarrow N\Delta\mu = N(\mu_l - \mu_v) = -N k_b T \ln S, \quad S = \overset{\text{vapor pressure}}{P}/\underset{\text{equilibrium vapor pressure}}{P_e}$$

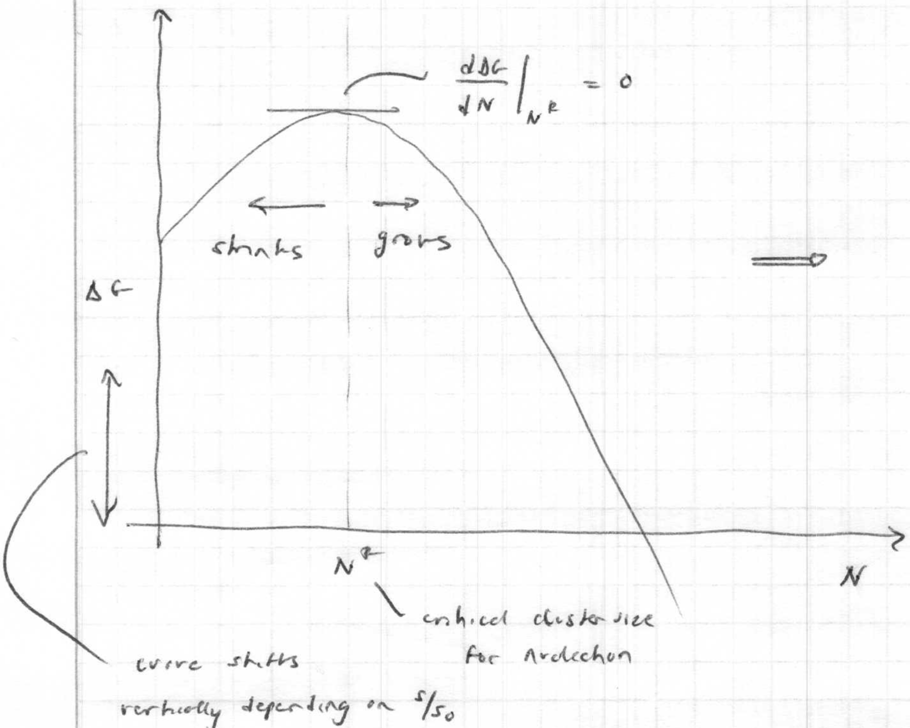
(assuming an ideal vapor)

$$\Rightarrow 4\pi R^2 \gamma = \gamma \cdot 4\pi \left(\frac{3a_v}{4\pi}\right)^{2/3} N^{2/3}, \quad \text{from } V = \frac{4}{3}\pi R^3 = a_v N$$

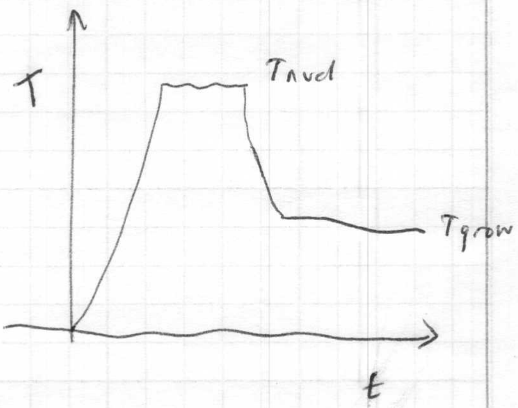
$$\Rightarrow R = \left(\frac{3a_v N}{4\pi}\right)^{1/3}$$

so, $\Delta G = -N k_b T \ln S + \gamma 4\pi \left(\frac{3a_v}{4\pi}\right)^{2/3} N^{2/3}$ $\qquad SA = 4\pi R^2 = 4\pi\left(\frac{3a_v}{4\pi}\right)^{2/3} N^{2/3}$

$\Delta G = W =$ reversible work needed to form a cluster of N atoms.



$\Longrightarrow$



what is the critical cluster size N^*?

solve $\frac{d\Delta G}{dN} = 0$: $-k_b T \ln S + \frac{4\pi\gamma}{3}\left(\frac{3a_v}{4\pi}\right)^{2/3} N^{-1/3} = 0$

$$\Longrightarrow \underline{N^* = \frac{32\pi\gamma^3 a_v^2}{3(k_b T \ln S)^3}}$$

$$R^* = \left(\frac{3a_v N^*}{4\pi}\right)^{1/3} \Longrightarrow \underline{R^* = \frac{2\gamma a_v}{kT\ln S}}$$

barrier height = nucleation energy : $\Delta G(R^*) = \Delta G(N^*)$

$$\underline{\Delta G^* = \frac{16\pi\gamma^3 a_v^2}{3\left((k_b T)(\ln S)\right)^3}}$$

S is really a distribution because of local fluctuations in concentration if $S\uparrow$, $\Delta G\downarrow \Rightarrow N^*\downarrow$

if $T\uparrow$, $\Delta G\downarrow \Rightarrow N^*\downarrow$ $\Rightarrow$ want to nucleate at high temp then cool rapidly

can also change concentrations /
capping chemistries, etc.

(same goal - to separate events)

examples: metals above bulk melting point

Al : 1472 K   temperatures at which $P_e = 0.01$ Torr

Fe : 1678 $P_e = P_0 e^{-E/kT}$

Ag : 1262

see curves for metals, $S = 50$, $P = 0.5$ Torr, $P_e = 0.01$ Torr

part 2: growth: focusing and broadening of size distributions based on diffusion and precipitation in solution

starting with Sugimoto fig. 2, showing diffusion to a particle in solution, we state that

$$\underbrace{J}_{\text{monomer flux}} = 4\pi x^2 \underbrace{D}_{\text{diffusion coefficient}} \frac{dc}{dx} \leftarrow \text{concentration of precursor ("monomer")}$$

$$\frac{J}{4\pi D}\int_{r+\delta}^{r}\frac{dr}{r^2} = \int_{c_b}^{c_i} dc \Rightarrow \frac{J}{4\pi D}\left(-\frac{1}{r}\right)_{r+\delta}^{r} = \overset{\text{interface}}{c_i} - \overset{\text{bulk}}{c_b}$$

$$\Rightarrow \frac{J}{4\pi D}\left(\frac{1}{r} - \frac{1}{r+\delta}\right) = c_i - c_b$$

$$\frac{J}{4\pi D}\left(\frac{\delta}{r(r+\delta)}\right) = c_b - c_i$$

$$\Rightarrow \underline{J = \frac{4\pi D r(r+\delta)}{\delta}(c_b - c_i)}$$ governs diffusion of monomers to surface.

For the surface reaction,

$$J = 4\pi r^2 k (c_i - c_e)$$

equilibrium concentration (solubility)

rate constant (1st-order)

therefore :
$$\frac{c_i - c_e}{c_b - c_i} = \frac{D}{kr}\left(1 + \frac{r}{\delta}\right)$$

<u>case i</u> : diffusion controlled growth : $c_i = c_e$, if $D \ll kr$

means the surface concentration is in equilibrium w/ solution

so $$J = \frac{4\pi D r(r+\delta)}{\delta}(c_b - c_e) = \frac{4\pi r^2}{V_m}\frac{dr}{dt}$$

molar volume

$$\frac{dr}{dt} = \frac{DV_m}{r^2}\left(\frac{r+\delta}{\delta}\right)(c_b - c_e)$$

$$\underline{\frac{dr}{dt} = DV_m\left(\frac{1}{r} + \frac{1}{\delta}\right)(c_b - c_e)}$$

thus : $c_b > c_e$: growth

$c_b < c_e$: shrinkage (dissolves)

if $r \uparrow$, $\frac{dr}{dt} \downarrow$: bigger particles grow more slowly

case ii : reaction controlled growth

if $D \gg kr$, then $c_b \approx c_i$ and growth is limited by surface reaction rate

so $\frac{dr}{dt} = kv_m(c_b - c_e)$

$\Rightarrow \frac{dr}{dt}$ is independent of particle size

however, $(c_b - c_e)$ is not independent of particle size

let's see how the size distribution evolves

recall earlier we derived that $r^* = \frac{2\gamma av}{kT\ln S'}$

$$\ln S' = P/P_e = \exp\left(\frac{2\gamma av}{kTr^*}\right)$$

$$\Rightarrow \quad c_e = c_\infty \exp\left(\frac{2\gamma av}{kTr}\right)$$

$$c_b = c_\infty \exp\left(\frac{2\gamma av}{kT\boxed{r^*}}\right)$$

c_∞ = solubility of solid w/ infinite dimensions ("equilibrium vapor pressure") [dimensionless]

r^* = particle radius in equilibrium with bulk solution

if $2\gamma av \ll kTr$, approximate

$$c_e \approx c_\infty\left(1 + \frac{2\gamma av}{kTr}\right)$$

$$c_b \approx c_\infty\left(1 + \frac{2\gamma av}{kTr^*}\right)$$

so, $c_b - c_e = \frac{c_\infty \cdot 2\gamma a_v}{kT}\left(\frac{1}{r^*} - \frac{1}{r}\right)$

for diffusion controlled growth, $\delta >> r$

so $\frac{dr}{dt} = \underbrace{D v_M}_{= N_A a_v}\left(\frac{1}{r} + \cancel{\frac{1}{\delta}}\right)\underbrace{(c_b - c_e)}_{\text{what we just calculated}}$

$\Rightarrow \frac{dr}{dt} = D N_A a_v \cdot c_\infty \cdot \frac{2\gamma a_v}{kT}\left(\frac{1}{r}\right)\left(1/r^* - 1/r\right)$

choose $k_D = \frac{2\gamma D N_A a_v^2}{kT} c_\infty$

$\Rightarrow \underbrace{\frac{dr}{dt} = \frac{k_D}{r}\left(\frac{1}{r^*} - \frac{1}{r}\right)}$ $\left.\begin{array}{l} r > r^* \text{ grows} \\ r < r^* \text{ shrinks} \end{array}\right\}$ ostwald ripening

let's assign $\bar{r}$ = mean r, Δr = stdev of r

assuming constant r^*, we can show that $\Delta r \approx 1 + \delta/\bar{r}$

can be shown that

$\frac{d(\Delta r)}{dt} = \frac{k_D \Delta r}{\tilde{r}^2}\left(\frac{2}{\tilde{r}} - \frac{1}{r^*}\right)$, thus,

$\frac{d(\Delta r)}{dt} > 0$ if $\frac{\tilde{r}}{r^*} < 2$ $\Rightarrow$ broadens (Δr decreases)

$\frac{d(\Delta r)}{dt} < 0$ if $\frac{\tilde{r}}{r^*} > 2$ $\Rightarrow$ focuses (Δr increases)

$\Rightarrow$ see plot on side; confirmed experimentally by Peng

for reaction-controlled growth,

$$\frac{dr}{dt} = K_R\left(\frac{1}{r^*} - \frac{1}{r}\right), \quad K_R = \frac{2\gamma k N_a a_v^2 c_\infty}{k_b T}$$

$$\Rightarrow \frac{d\Delta r}{dt} = \frac{K_R \Delta r}{\bar{r}^2} \longrightarrow \text{always grows (at a decreasing rate)}$$