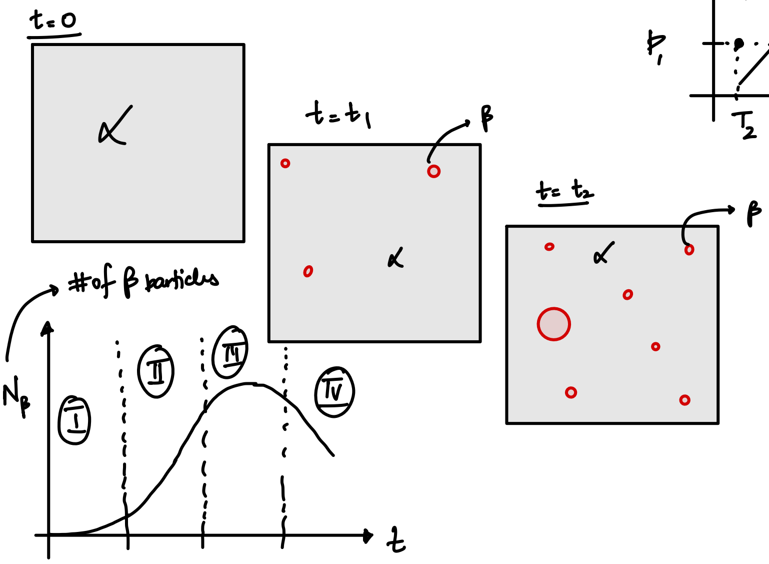
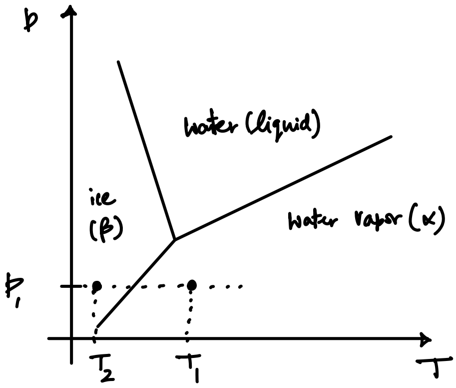
Homogeneous Nucleation

Consider a single component material, say water
Say we cool down the water vapor from a temperature of $T_1 \rightarrow T_2$ @ a pressure p_1





4-stages of the phase transformation

I $\longrightarrow$ Incubation; α is metastable, small clusters of the β phase are formed and decomposed.

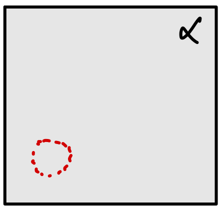
II $\longrightarrow$ Quasi steady state nucleation; stable nuclei are continuously produced.

III $\longrightarrow$ Decreased rate of nucleation; typically due to a decrease in supersaturation.

IV $\longrightarrow$ late stages; Nucleation of new particles is negligible; Existing nuclei grow

We will primarily focus on I & II

Classical Theory of Nucleation



Say there are N particles of α

$\alpha \longrightarrow \beta$ will result in a free energy change.

STEPS TO COMPUTE THE FREE ENERGY CHANGE

① Pick n particles that form a cluster and remove them $\Rightarrow$ forms a void in α

② rearrange the n particles to form β

③ Insert the β phase back into α

$$\Delta G_{cluster} = \Delta G_{bulk} + \Delta G_{interfacial} + \Delta G_{strain}$$

ΔG_{bulk}: bulk free energy change due to transition from $\alpha \rightarrow \beta$

$\Delta G_{interfacial}$: energy penalty due to interface between α & β

ΔG_{strain}: neglect for now

ASSUME:

① Spherical cluster with radius r

② Isotropic interfacial energy

③ No strain energy

$$\Delta G_{bulk} = V_{cluster}\, \Delta g^{\alpha\to\beta}$$

$\Delta g^{\alpha\to\beta}$: free energy change / unit volume.

$$= \left(\frac{4}{3}\pi r^3\right) \Delta g^{\alpha\to\beta}$$

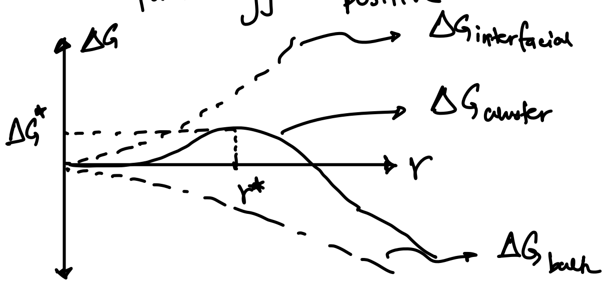
$$\Delta G_{interfacial} = \left(4\pi r^2\right)\gamma$$

γ: surface energy per unit area

$$\Delta G_{cluster} = \frac{4}{3}\pi r^3 \Delta g^{\alpha\to\beta} + 4\pi r^2 \gamma$$

when $T < T^{\alpha\to\beta}$; α is metastable and $\Delta g^{\alpha\to\beta} < 0$

surface energy is positive



$\Delta G^*(r^*, T)$ is the free energy @ the critical radius (r^*) beyond which the free energy decreases with increasing size.

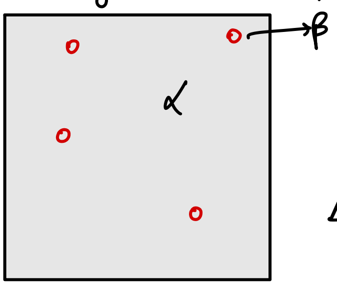
$$\left.\frac{\partial \Delta G_{cluster}}{\partial r}\right|_{r=r^*} = 0 = 4\pi r^*\left[\Delta g^{\alpha\to\beta} r^* + 2\gamma\right]$$

$$r^* = \begin{cases} 0, \\ \dfrac{-2\gamma}{\Delta g^{\alpha\to\beta}} \end{cases}$$

$\boxed{r^* \downarrow \text{ as } \gamma \downarrow \text{ or } \Delta g^{\alpha\to\beta} \text{ becomes more negative}}$

$$\boxed{\Delta G^*(r^*, T) = \frac{16\pi\gamma^3}{3(\Delta g^{\alpha\to\beta})^2}}$$

* In a real system at a temperature $T > T^{\alpha\to\beta}$



clusters of β will stochastically appear and disappear

Let a cluster have c atoms

surface area of the cluster $A \propto \eta c^{2/3}$ — shape factor

$$\Delta G(c) = c\Delta g^{\alpha\to\beta} + \eta c^{2/3}\gamma$$

$\Delta g^{\alpha\to\beta}$: bulk free energy per atom

γ: surface energy.

Let there be N_c clusters of size c and $\mathcal{N}$ total atoms

\# of atoms in the β phase $= \sum_c N_c c = N_\beta$

\# of atoms in the α phase $= \mathcal{N} - N_\beta = \mathcal{N} - \sum_c N_c c = N_\alpha$

Free energy of the system:

$$\Delta G = \underbrace{\sum_c N_c \Delta G(c)}_{\text{free energy change to form } \beta} + \underbrace{k_B T\left[N_\alpha \log\left(\frac{N_\alpha}{N_\alpha + \sum_c N_c}\right) + \sum_c N_c \log\left(\frac{N_c}{N_\alpha + \sum N_c}\right)\right]}_{\text{Configurational entropy of arranging } N_c\ \beta \text{ clusters and } N_\alpha\ \alpha \text{ atoms.}}$$

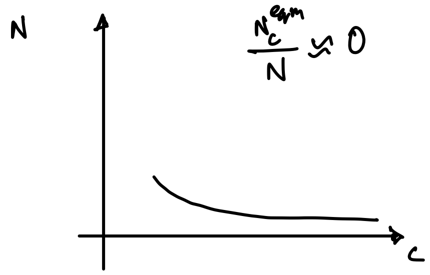
Notice $\Delta G(\{N_c\})$ $\longrightarrow$ # of clusters of size c

@ eq^m:

$$\frac{\partial \Delta G}{\partial N_c} = 0 \Rightarrow \boxed{\frac{N_c^{eqm}}{N} \approx \exp\left(-\frac{\Delta G(c)}{k_B T}\right)}$$

when $T > T^{\alpha\to\beta}$; $\Delta G(c) > 0$

$$\frac{N_c^{eqm}}{N} \approx 0$$



* Consider now a scenario where α is metastable $\Rightarrow T < T^{\alpha\to\beta}$

$J_c(t)$ = rate of growth or depletion of a cluster of size c to a cluster of size c+1

$$J_c(t) = \beta_c N_c(t) - \alpha_{c+1} N_{c+1}(t)$$

α_{c+1} → rate @ which an atom detachs from the cluster to α

β_c ↳ rate @ which single atoms attach to the clusters of size c from α

ASSUME: no clusters beyond a size C_{max} are allowed to grow. $c_{max} \gg c^*$ → critical cluster size

At eq^m: $$\frac{N_c^{eq}}{N} = \exp\left(-\frac{\Delta G(c)}{k_B T}\right)$$

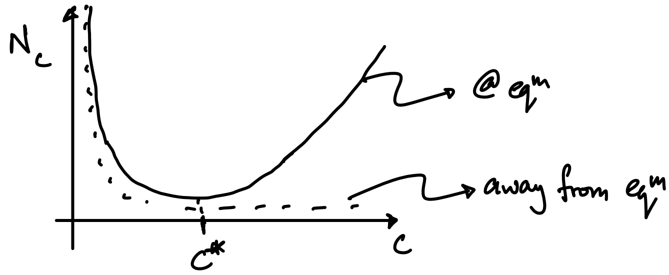
During Stage I: after eq^m is reached $\Rightarrow J_c(t) = 0 \longrightarrow$ the distribution should be stationary.

$$\beta_c N_c^{eq} - \alpha_{c+1} N_{c+1}^{eq} = 0 \Rightarrow \alpha_{c+1} = \beta_c\left(\frac{N_c^{eq}}{N_{c+1}^{eq}}\right)$$

$$J_c(t) = \beta_c N_c^{eq}\left[\frac{N_c(t)}{N_c^{eq}} - \frac{N_{c+1}(t)}{N_{c+1}^{eq}}\right]$$

$$\frac{d}{dc}\left(\frac{N_c(t)}{N_c^{eq}}\right) \approx \frac{N_{c+1}(t)}{N_{c+1}^{eq}} - \frac{N_c(t)}{N_c^{eq}}$$

$$\boxed{J_c(t) = -\beta_c N_c^{eq} \frac{d}{dc}\left(\frac{N_c(t)}{N_c^{eq}}\right)}$$



During stage II: under quasi-steady state $\Rightarrow J_c(t) = J \longrightarrow$ constant rate that is independent of time & cluster size

$$J = -\beta_c N \exp\left(-\frac{\Delta G(c)}{k_B T}\right) \frac{d}{dc}\left(\frac{N_c(t)}{N_c^{eq}}\right)$$

$$\Rightarrow \quad -\frac{1}{J}\int_1^0 d\left(\frac{N_c}{N_c^{eq}}\right) = \frac{1}{N}\int_1^\infty \frac{1}{\beta_c}\exp\left(\frac{\Delta G(c)}{k_B T}\right) dc$$

(i) when c is small; $\frac{N_c}{N_c^{eq}} \approx 1 \longrightarrow$ small clusters are easy to form and independent of time, should be close to eq^m

(ii) when c is large; $N_c/N_c^{eq} \to 0 \longrightarrow$ only a few clusters will grow past critical cluster size

APPROXIMATE: $\beta_c \approx \beta_{c^*} = \text{Constant} = \beta$

$$\Delta G(c) \approx \Delta G(c^*) + \frac{(c-c^*)^2}{2} \left.\frac{\partial^2 \Delta G(c)}{\partial c^2}\right|_{c=c^*} + \text{higher order terms.}$$

$$\left.\frac{\partial^2 \Delta G(c)}{\partial c^2}\right|_{c=c^*} = -\frac{2}{3}\frac{\Delta G(c^*)}{(c^*)^2}$$

$$-\frac{1}{J}\int_1^0 d\left(\frac{N_c}{N_c^{eq}}\right) = \frac{1}{N\beta \exp\left(-\frac{\Delta G(c^*)}{k_B T}\right)} \int_1^\infty \exp\left(-\frac{(c-c^*)^2}{(c^*)^2}\frac{\Delta G(c^*)}{3k_B T}\right) dc$$

$1 \rightarrow$ replace with $-\infty$ (has negligible impact on the integral)

RHS is a Gaussian integral

$$\Rightarrow J = \underbrace{\left(\frac{\Delta G(c^*)}{3\pi c^{*2} k_B T}\right)^{1/2}}_{\text{Zeldovich factor } (Z)} \beta N \exp\left(-\frac{\Delta G(c^*)}{k_B T}\right)$$

$$\boxed{J = Z \beta N \exp\left(-\frac{\Delta G(c^*)}{k_B T}\right)}$$

$Z \sim 0.1$

$J \rightarrow$ the rate of formation of clusters of size c^* is smaller than the value we would anticipate if clusters CANNOT decrease in size.