Nucleation Kinetics

The most interesting in Nature is the existence of the world

The most interesting in the world is the **birth** *of new worlds in the heart of the old one or at the interface of the two old worlds*

The most interesting in the birth is **the initial stage**

Initial stage usually starts with **nucleation** *of new phases*

Nucleation is a miracle when the embryo grow to a critical size opposite the Second Law of Thermodynamics

Consider a closed system consisting of M atoms (or molecules). The thermodynamic potential of old phase is $G_{old} = M\boldsymbol{m}_{old}$. After a formation of an n atomic cluster of the new phase the Thermodynamic potential becomes

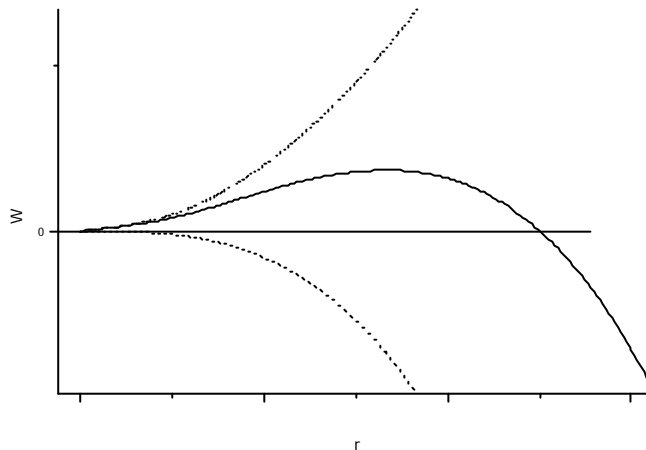$G_{new} = (M-n)\boldsymbol{m}_{old} + n\boldsymbol{m}_{new} + G_{ex}(n)$

The work of formation of the cluster is

$$W(n) = -n\boldsymbol{Dm}_{\infty} + G_{ex}(n)$$

In isotropic approximation

$$W(r) = -\frac{4\boldsymbol{p}r^3}{3v}\Delta\boldsymbol{m}_{\infty} + 4\boldsymbol{p}r^2\boldsymbol{s}$$

$$W_{max} = ? \qquad r_{max} = ?$$

$$\left(\frac{\partial W}{\partial r}\right)_{r=r_{max}} = 8\boldsymbol{p}r_{max}\boldsymbol{s} - \frac{4\boldsymbol{p}r_{max}^2}{v}\boldsymbol{Dm}_{\infty} = 0$$

$$r_{max} = \frac{2\boldsymbol{s}v}{\boldsymbol{Dm}_{\infty}}$$

This gives the melting point $T_m(r)$ of small clusters:

$$\Delta\boldsymbol{m} \approx H_m(T_m - T) = \frac{2\boldsymbol{s}v}{r}$$

For any nucleus:

$$W = \sum_i \boldsymbol{s}_i O_i - n\boldsymbol{Dm}_{\infty}$$

The equilibrium form rule of Wulff states:

$$\frac{\boldsymbol{s}_i}{r_i} = \frac{\Delta \boldsymbol{m}_{\infty}}{2v} \quad ; \quad n = \frac{V}{v} = \frac{1}{3}\sum \frac{O_i r_i}{v} \quad \text{(sum of pyramids)}$$

and

$$r_i = \frac{2\boldsymbol{s}_i V}{\boldsymbol{D}\boldsymbol{m}_{\infty}}$$

so that:

$$W = \sum \boldsymbol{s}_i O_i - \frac{\boldsymbol{D}\boldsymbol{m}_{\infty}}{3}\sum \frac{O_i r_i}{v} = \sum \boldsymbol{s}_i O_i - \frac{\boldsymbol{D}\boldsymbol{m}_{\infty}}{3}\sum \frac{2vO_i \boldsymbol{s}_i}{v\boldsymbol{D}\boldsymbol{m}_{\infty}} =$$

$$= \sum \boldsymbol{s}_i O_i - \frac{2}{3}\sum \boldsymbol{s}_i O_i = \frac{1}{3}\sum \boldsymbol{s}_i O_i$$

$$W = \frac{1}{3}\sum \boldsymbol{s}_i O_i$$

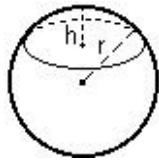For two dimensional nucleus on flat crystalline surface

$$W_2 = \frac{1}{2}F\,\hat{e}$$

Heterogeneous nucleation
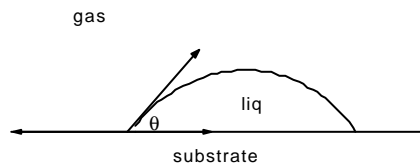
$$\sigma_{s/g} = \sigma_{s/l} + \sigma_{l/g}\cos\theta$$

$$\boldsymbol{D}\boldsymbol{s} = \boldsymbol{s}\cos\boldsymbol{q}$$

Volume: $\frac{1}{3}\cdot\pi\cdot h^2\cdot(3\cdot r - h)$

Surface area: $2\cdot\pi\cdot r\cdot h$

$$h = r(1 - \cos\mathbf{q}) \quad ; \qquad V = \frac{1}{3}\mathbf{p}r^3(1 - \cos\mathbf{q})^2(2 + \cos\mathbf{q})$$

$$S_1 = 2\mathbf{p}r^2(1 - \cos\mathbf{q}) \quad ; \quad S_2 = \mathbf{p}r^2(1 - \cos^2\mathbf{q})$$

$$W = \left(S_1 + S_2(1 - \cos^2\mathbf{q})\cos\mathbf{q}\right)\mathbf{s} - \frac{V}{v}\Delta\mathbf{m}(r)$$

$$W^* = W_o\Phi \quad ; \quad \Phi = \frac{1}{2} - \frac{3}{4}\cos\mathbf{q} + \frac{1}{4}\cos^2\mathbf{q}$$

According to Kaischew $\quad \Phi = \dfrac{V_c^*}{V_c}$

Consider a small part of the system, consisting of x "atoms" . According to the Bolzman's law the probability w is at a state different from the equilibrium one has, in Einstein formulation, the form: $\quad w = e^{\frac{\mathbf{D}S}{k}}$

In isolated system ($\mathbf{D}U=0$) a critical nucleus can be formed by doing a work $W_c=Q_c=T\mathbf{D}S_c$

The probability that a critical nucleus is formed somewhere in the system is: $w_c = W e^{-\frac{W_c}{kT}}$ Here we consider the system as consisting of $W = N/x_c$ independent parts.

On the other hand, taking into account the kinetics of the process, w_c is equal to the frequency J' of appearance of critical nuclei and their life time q, $w_c = J' q$ So that $J' = \dfrac{N}{x_c q} e^{-\frac{W_c}{kT}}$

From $J = J'/2$ the nucleation rate becomes

$$ J = K e^{-\frac{W_c}{kT}} \; ; \quad K = \frac{N}{2 x_c q} $$

Up to here the derivation was quite generalized and does not give an idea how the process proceeds. The value of K cannot be estimated without detailed model.

Phenomenological and kinetic description of nucleation kinetics:

We consider a phase ,A, which is brought to conditions *(p,T, …)* at which stable is phase ,B, $(m_A > m_B)$. As soon as the phase A is metastable, nuclei of phase B start to appear.

The approach was first developed by Farkas following an idea of Scilard

$$ a + a \ll b_2 $$
$$ b_2 + a \ll b_3 $$
$$ b_3 + a \ll b_4 $$
$$ .... $$
$$ b_x + a \ll b_{x+1} $$
$$ .... $$

Here a is a building unit of phase A , b_x is a nucleus (consisting of x building units) of phase B. In the model it is assumed that nuclei are not interacting with each other. Moreover, strictly speaking, the scheme should begin starting a size $x_o > 1$ that is capable to keep information about the new

structure. This is to say it should include at least several elementary cells. Only nuclei larger a given critical size x_c can grow spontaneously.

At size g clusters are removed from the system and equivalent number of monomers is returned back

The main task of the theory is to find the nucleation rate at any size and time $J(x,t)$.

The process can be completely described using a function $Z(x,t)$ that gives the number of nuclei of size x at moment t.
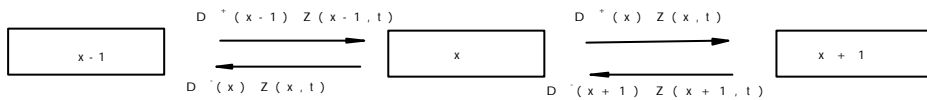
The differential equation that correspond to it is:

$$\frac{\partial Z(x,t)}{\partial t} = D^+(x-1)Z(x-1,t) + D^-(x+1)Z(x+1,t) - D^+(x)Z(x,t) - D^-(x)Z(x,t)$$

After sufficiently long time a steady state is established. A stationary distribution requires that $\frac{dZ}{dt} = 0$ so that

$$D^+(x-1)Z(x-1) - D^-(x)Z(x) = D^-(x+1)Z(x+1) - D^+(x)Z(x,t) = J_{st}$$

There is a detailed balance for $J_{st}=0$, i.e. the number of nuclei transiting to upper class is equal to the number of nuclei coming from it.

$$D^-(x) = \frac{D^+(x-1)Z_e(x-1)}{Z_e(x)}$$

The equilibrium size distribution of nuclei is derived by Frenkel as:

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$$Z_e(x) = N_1 \, exp\left[-\frac{DG(x)}{kT}\right] \quad , \quad N_1 \gg N$$

Steady state solution

In the steady state , the cluster size distribution is not changed with time. Therefore,

$J(x-1)=J(x)$ holds for all sizes under consideration ($2 \pounds x \pounds g-1$) . The following system is obtained

$$D_1^+N_1 - D_2^-N_2 = J_{st}$$
$$D_2^+N_2 - D_3^-N_3 = J_{st}$$
$$D_3^+N_3 - D_4^-N_4 = J_{st}$$

$$\ldots\ldots\ldots\ldots\ldots$$

$$D_{g-2}^+N_{g-2} - D_{g-1}^-N_{g-1} = J_{st}$$
$$D_{g-1}^+N_{g-1} = 0$$

A multiplication of second of these equations with D_2^-/D_2^+, *the third with* $(D_2^-/D_2^+)(D_3^-/D_3^+)$ *etc.* and subsequent addition of all equations (the intermediate terms are eliminated)

$$J = \cfrac{D_1^+ N_1}{\left(1 + \sum_{x=2}^{g-1} \cfrac{D_2^- D_3^- D4...D_x^-}{D_2^+ D_3^+ D_4^+...D_x^+}\right)}$$

Note that $\displaystyle\sum_{x=2}^{g-1} \frac{D_2^- D_3^- D4...D_x^-}{D_2^+ D_3^+ D_4^+...D_x^+} = \prod e^{\frac{\Delta_i}{kT}} = e^{\frac{W}{kT}}$

Non Steady state solution

For relatively large nuclei the discrete equation is transformed to differential:

$$\frac{\partial Z(x,t)}{\partial t} = D^+(x-1)Z_e(x-1)\left[\frac{Z(x-1,t)}{Z_e(x-1)} - \frac{Z(x,t)}{Z_e(x,t)}\right] - D^+(x)Z_e(x)\left[\frac{Z(x,t)}{Z_e(x)} - \frac{Z(x+1,t)}{Z_e(x)}\right]$$

Considering x as continuous variable

$$\frac{\partial Z(x,t)}{\partial t} = -D^+(x-1)Z_e(x-1)\frac{\partial}{\partial x}\left[\frac{Z(x-1,t)}{Z_e(x-1)}\right] + D^+(x)Z_e(x)\frac{\partial}{\partial x}\left[\frac{Z(x,t)}{Z_e(x)}\right]$$

Taking into account truncated Taylor series

$$\frac{\partial Z(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{ D(x)Z_e(x)\frac{\partial}{\partial x}\left[\frac{Z(x,t)}{Z_e(x)}\right]\right\} \quad \text{This is a parabolic type equation.}$$

It requires one initial and two boundary conditions

Initial condition $Z(x,0)=0$, $x>1$

First boundary condition: $Z(1,t)=Z_e(1)$

II boundary condition: $Z(N,t)=0$ *i.e. there are no nuclei with $x>>x_c$*

$$J_{st} = D_c Z_c \sqrt{-\frac{1}{2pkT\left(\frac{\partial^2 \Delta G(x)}{\partial x^2}\right)_{x-x_c}}} = D_c N \sqrt{-\frac{1}{2pkT\left(\frac{\partial^2 \Delta G(x)}{\partial x^2}\right)_{x-x_c}}} \exp\left(-\frac{W_c}{kT}\right)$$

Zeldovich: $J(t) = J_{st}\, exp\left(-\frac{t}{t}\right)$, $t = -\dfrac{8kT}{p^2 D_c\left(\dfrac{\partial^2 DG(x)}{\partial x^2}\right)_{x-x_c}}$

The Zeldovich parameter is: $\mathbf{Z} = \sqrt{-\dfrac{1}{2pkT\left(\dfrac{\partial^2 \Delta G(x)}{\partial x^2}\right)_{x-x_c}}} = \dfrac{1}{n_c}\sqrt{\dfrac{W_c}{3pkT}}$
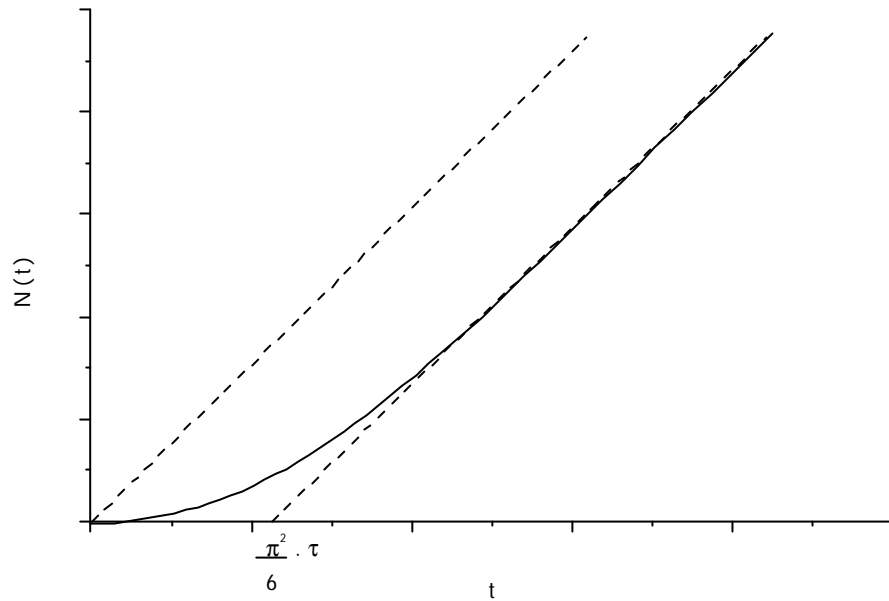
Where n_c is the number of atoms in critical nucleus

$$J_{st} = Z D_c N_c$$

$$N_c = N\exp\left(-\frac{W_c}{kT}\right); \qquad D_c = \frac{OkT}{d_o^5 h}; \qquad t = \frac{4}{p^3 Z^2 D_c}$$

$$J_{st} = \frac{3kT}{d_o^5 h}\sqrt{\frac{4ps}{3kT}}\exp\left(-\frac{16ps^3 V^2}{3kT\,\Delta m^2}\right)$$

Kashchiev: $J(t) = J_{st}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-n^2\frac{t}{t}}\right]$

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For crystallization in undercooled melts, Gutzow has simplified the expression for the time lag to be:

$$\boldsymbol{t}_{ind} = 2d_o^5 \frac{\boldsymbol{hs}}{\boldsymbol{a}(\boldsymbol{Dm})^2}$$

Useful formulae to remember:

$$n_c = \left(\frac{2\boldsymbol{p}\mathrm{d}_o^2 \boldsymbol{s}}{3\Delta\boldsymbol{m}}\right)^3$$

Stokes-Einstein $\quad D = \dfrac{kT}{\boldsymbol{h}\mathrm{d}_o}$

INFLUENCE OF STRESS ON NUCLEATION KINETICS

Degree of stress development depends on the ratio

$$q = \frac{t_{nuc}}{t_{rel}}$$

ASSUMPTION: **both the process of relaxation and the process of nucleation are controlled by the same kinetic coefficient – the bulk melt viscosity η**

If a stress energy Φ is developed $\quad m_{str} = \dfrac{\partial \Phi}{\partial n}$

$$r_c = \frac{2 s V_c}{\Delta m - m_{str}}$$

If stress relaxation can be neglected

$$\Phi_o = m_{st}^o n_c \quad ; \quad m_{st}^o = \frac{E d^2}{9(1 - g)} V_c$$

If the system can relax

$$\frac{d\Phi}{dt} = \left(\frac{\partial \Phi}{\partial t}\right)_{crys} - \frac{\Phi}{t_r}$$

$$m_{str}(t_{nuc}) = \frac{t_r}{t_{nuc}}\left(1 - e^{-\frac{t_{nuc}}{t_r}}\right)$$

$$\frac{t_{nuc}}{t_r} \approx \frac{T}{T_m}\frac{R}{\Delta S_m} n_c^{2/3}$$