A new theory of nucleation

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The classical nucleation and growth model is modified and it is shown that the concept of fluctuations, instability and surface energy is not needed and that (as applies for glass transition) nucleation is a common example of the kinetic theory of structural change processes, with a special driving force and a special property of the activation volume parameter. This last follows from explanation of diffusion tests. This new nucleation equation leads to a new vision on heterogeneous nucleation, applicable to solids. The equation also provides, as necessary, the theoretical equation of the thus far empirical C-curves of the time-temperature-transformation diagrams (TTT-diagrams).

Keywords: characterization; nucleation; solidification; stresses; reaction kinetics

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1. Introduction

Based on the kinetics equation for structural change of Appendix 1, which by its form is e.g. able to explain transient nucleation and structural relaxation of glasses, a new theory of nucleation is derived starting by extension and correction of the classical model. Therefore, the essence of the classical model is first discussed in Section 2.

In Section 3, based on general conditions, the derivation of the equilibrium concentration of the embryos depending on size is given. Herewith information is obtained on the nucleation mechanism and on the driving force for embryo formation. The classical distinction between volume free energy and temperature independent surface free energy of the embryo is shown to be superfluous and questionable.

In Section 4, heterogeneous nucleation is derived which generally applies, also for solids. The derivation is based on continuity condition of the growth rate, replacing the classical model of surface energy, in the form of nonexistent surface stresses in solids.

In Appendix 3, based on diffusion tests, the theoretical explanation of the different empirical equations by their different activation volume parameters is given, based on the derivation of the empirical power law equation in Appendix 2. Herewith the special form of the activation volume term of the driving force of nucleation is found as applied in Section 5.

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It is shown in Section 5, that the special expression of the activation volume of the basic rate equation explains the data and nucleation behaviour (as well for homogeneous as for heterogeneous nucleation by one equation). As discussed in Section 6, this rate equation shows the well known increase of the rate at the increase of undercooling up to a maximum value and then a decrease of the rate at larger undercooling steps giving thus a theoretical equation and explanation of the C-curves of the time-temperature-transformation diagrams (TTT-diagrams).

2. Discussion of the classical nucleation model

Homogeneous nucleation is, according to the classical nucleation theory, the change in free energy of the system ΔE_e due to the formation of a spherical phase cluster of radius R:

$$\Delta E_e = (4/3)\pi R^3 \Delta g + 4\pi R^2 \gamma \qquad (1)$$

where Δg is the change of the free energy per unit volume and γ the free energy of the interface between parent phase and fluctuation, which is assumed to be constant, independent of the temperature. When $\Delta g < 0$, ΔE_e of Equation (1) has a maximum at the critical size of R_c and fluctuations with $R < R_c$ are more probable to shrink and dissolve than to grow because of the decrease of the free energy, while the fluctations of $R > R_c$ grow spontaneously, also because of the decrease of the free energy. The critical value $R = R_c$, follows from:

$$\mathrm{d}(\Delta E)/\mathrm{d}R = 0, \text{or according to Equation (1):}$$
$$4\pi R^2 \Delta g + 8\pi R \gamma = 0 \text{ or } R_c = -2\gamma/\Delta g. \qquad (2)$$

Substitution of R_c of Equation (2) into Equation (1) gives the critical value for nucleation:

$$\Delta E_c = (16\pi\gamma^3)/(3\Delta g^2). \qquad (3)$$

Because Δg has the form $\Delta g = \Delta h - T\Delta s = \Delta s(T_e - T)$ and γ is assumed to be constant, with respect to temperature, Equation (3) gets the empirical form of $\Delta E_c = C_2/(T_e - T)^2$. In the literature, e.g. [1–4], also other expressions for ΔE_c are chosen to adapt better to data.

The general thermodynamic reasoning on shrinking or grow gives no explanation of behaviour because it may happen in infinite ways and only knowledge of the mechanism provides predictable behaviour. For instance, it should be explained how a single fluctuation in solids transformation may exist involving so many molecules that a distinction is possible between a separate constant surface energy and a volume energy, up to the size of the critical embryo. As an answer the modification was proposed to regard embryo formation as result of successive reactions. In reference [5], e.g. embryo formation is regarded to occur by a large number of successive bimolecular reactions (explaining also why specific activation energies have to be applied) as follows:
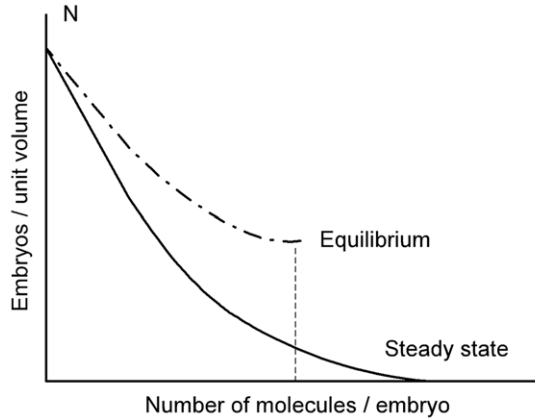
$$O_1 + O_1 \rightleftharpoons O_2 \text{ and } O_2 + O_1 \rightleftharpoons O_3 \text{ etc. summed up to } nO_1 \rightleftharpoons O_n.$$
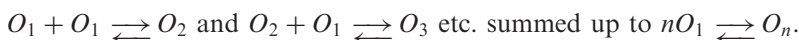
Figure 1. Concentration of embryos depending on size.

For equilibrium of these reactions is for n_i, the number of embryos per unit volume containing i molecules each:

$$\exp(-\Delta E_i/kT) = \frac{n_i/(n_1 + \Sigma n_i)}{n_1/(n_1 + \Sigma n_i)^i} \approx n_i/n_1 \approx n_i/n \tag{4}$$

because $\Sigma n_i \ll n_1 \approx n$, where n is the total number per unit volume. ΔE_i follows from Equations (1) and (4) similar as the dash-dot line in Figure 1. Thus, the number of embryos per unit volume, which get converted from size i to size $(i+1)$, is the same for all values of i at the same conversion rate equal to the nucleation rate. The amount of embryos n_i is constant within each size but decreases by the increase of R.

At nucleation the stationary case is regarded, determined by the rate at nucleation of the critical embryo, the nucleus. To explain Equation (5), which has the empirically found form of a forward reaction only at nucleation, it was assumed that for small embryos, the concentration is about the equilibrium concentration $n_{i,e}$. For large sizes the concentration was assumed to be far below the equilibrium value and to be zero for $i \to \infty$ (Figure 1), loosing therefore its backwards reaction term. This apparent forward nucleation rate thus is assumed to be:

$$\dot{n} = \nu n \exp((-\Delta E_t + \Delta E_c)/kT) \tag{5}$$

in agreement with measurements. In Equation (5), ΔE_t is the energy barrier for transfer of atoms across the interface for nucleation at frequency ν and ΔE_c, the driving force required for nucleus formation.

Substitution of Equation (3), with $\Delta g = \Delta s(T_e - T) = \Delta s \Delta T$, shows that Equation (5) has the form of:

$$\dot{n} = A_1 \exp(-A_2/(T_e - T)^2 = A_1 \exp(-A_2/\Delta T^2) \tag{6}$$

for homogeneous nucleation.

Analogous is for the step growth mechanism of Figure 2:

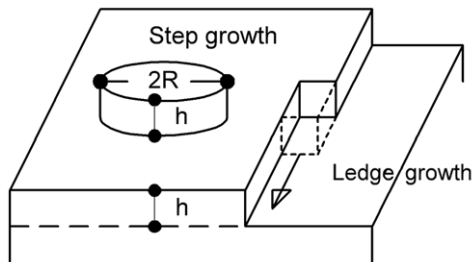$$\Delta E_e = \pi R^2 h \Delta g + 2\pi R h \gamma, \tag{7}$$

Figure 2. Step-growth after finished ledge growth.

leading by $d(\Delta E)/dR = 2\pi Rh\Delta g + 2\pi h\gamma = 0$ to the critical size for nucleation of:

$$R_c = -\gamma/\Delta g \tag{8}$$

and to the general form of Equation (5) of:

$$\dot{n} = A_1 \exp(-A_2/(T_e - T)). \tag{9}$$

This is regarded to be confirmed in Figure 3, by the empirical straight line of $\ln(\dot{n})$ against $1/(T_e - T)$ with the negative slope of $-A_2$. Equation (9) is given in Figure 3 by the drawn line.

Regarding the above given classical model the following remarks can be made:

(1) The free energy ΔE of Equation (1) is based on a constant γ independent of temperature. This is improbable because no real equilibrium, $\dot{n} = 0$, is possible at $T = T_e$ because Equations (2) and (3) show impossible infinite values of the nucleus dimensions (R_c) and of reaction heat to obtain equilibrium. Because $A_2/(T_e - T)$ has the form of $\Delta E/kT$ according to Equation (5), ΔE becomes infinite when $T = T_e$. This will be corrected to the right values in Section 5, by applying the right driving force and regarding the backwards reaction for small driving forces.

(2) Because the volume increase of the growing embryo, up to $(4/3)\pi R^3$ and the surface increase up to $4\pi R^2$ are coupled being one and the same process, γ and Δg should show one and the same temperature dependence. In fact thus one temperature dependent embryo growth process has to be regarded as is shown to apply in the following sections.

(3) The free energy representation by e.g. Equation (5): $\Delta E_c = (16\pi\gamma^3)/(3\Delta g^2)$, is confusing because it contains both specific heat and driving force values for volume and surface Δg and γ. Because of the identical growth of volume and of surface, the defined apparent surface energy γ should be proportional to Δg and ΔE_c. This follows directly from the elimination of γ, in stead of R_c, from Equations (1) and (2), giving:

$$\Delta E_c = -(2/3)\pi R_c^3 \Delta g, \tag{10}$$

the right form of the activation energy. Mathematically Equation (10) is identical to Equation (3).

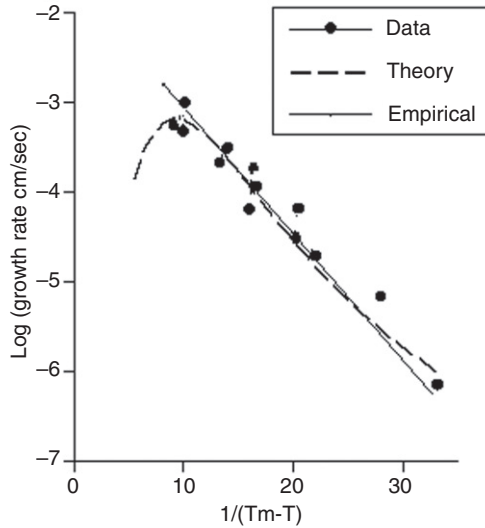As shown in Section 3, γ is a superfluous parameter.

Figure 3. Nucleation and growth rate of ice crystal.

3. Derivation of the embryo equilibrium concentration

Because ΔE_c is the highest for nucleation, the nucleation reaction is the slowest and determines the conversion rate of all embryos of the sequence of bimolecular reactions. The real rate and equilibrium equations of the classical model can be derived as follows. Because in Figure 1 the amount of embryos per unit volume n is a function of the radius R and growth is per step, the rate of sequential cylindrical embryo formation of Figure 2 is:

$$\mathrm{d}V/\mathrm{d}t = \dot{V} = \mathrm{d}(nh\pi R^2)/\mathrm{d}t = \left((\partial n/\partial R)h\pi R^2 + 2nh\pi R\right) \cdot \dot{R} \tag{11}$$

where the dot means derivative to the time t: $\dot{R} = \mathrm{d}R/\mathrm{d}t$. In this equation $\dot{R}$ or $\dot{V}$ follows from the kinetic diffusion equation in the form of Equation (A5) of Appendix 1.

   Equation (11) can be given per embryo to get the growth rate in number of molecules per embryo:

$$\dot{v} = \left(((\partial n/\partial R)/n)h\pi R^2 + 2h\pi R\right) \cdot \dot{R} = \left((\partial \ln n/\partial R) + 2\pi Rh/\pi R^2 h\right)h\pi R^2 \dot{R} \tag{12}$$

because n is constant, independent of time t at steady state. This can be written:

$$\dot{v} = ((\partial \ln n/\partial R) + A_e/V_e)h\pi R^2 \dot{R}. \tag{13}$$

   The determining reaction is the slowest reaction thus $\dot{v}$ is minimal at the nucleation step. This is the case when in Equation (13) A_e/V_e, the interface surface/embryo volume ratio, is minimal, as is satisfied by the spherical and by the cylindrical form of the step in Figure 2 and this minimum also applies when n is minimal, thus when $\partial \ln n/\partial R = 0$ at $R = R_c$. Then, $\partial \ln n/\partial R = -a + aR/R_c$ is required to have a real minimum at $R = R_c$, necessary for having an end-product of the successive reactions (being for other cases) the start of grain growth and necessary to have a negative slope for decreasing n at increase of

R (for $R < R_c$) and finally to have an exponential quadratic function in R, necessary for the possibility of an expression in specific free energy values. Thus integrated:

$$n = n_0 \exp(-aR + aR^2/(2R_c) - \Delta E_{t,d}/kT) = n_0 \exp\big((-\Delta E - \Delta E_{t,d})/kT\big)$$
$$= n_a \exp(-\Delta E/kT) \tag{14}$$

where n_a is the active reactant concentration and $\Delta E_{t,d}$ (independent of R) acts as resultant energy barrier for every migrating molecule between every embryo. Because R^2 is proportional to the total number of molecules per embryo, Equation (14) represents the equilibrium curve of the classical steady-state model, given in Figure 1. The positive term $aR^2/2R_c$ acts as driving force for embryo formation and by the term R^2 it is related to the specific volume free energy term Δg (with $\Delta \bar{g}$ as absolute value of Δg) by: $aR^2/2R_c = \Delta E_d/kT = (\pi R^2 h \Delta \bar{g})/kT$. The negative term in R, related to the surface of the embryo as derivative of the volume term, gives: $-aR = -2\pi Rh\Delta \bar{g} R_c/kT$, where $R_c \Delta \bar{g}$ is the specific energy barrier for embryo formation, replacing constant γ of the classical model.

The same result is found by applying the classical volume and surface energy terms: $(\pi R^2 h \Delta \bar{g} - 2\pi Rh\gamma)/kT = aR^2/2R_c - aR$, giving $a = 2\pi R_c h \Delta \bar{g}/kT$ and $\gamma = R_c \Delta \bar{g}$.

Thus ΔE of Equation (14) is: $\Delta E = -\pi R^2 h \Delta \bar{g} + 2\pi R R_c h \Delta \bar{g}$

For $R = R_c$, the critical embryo for nucleation, the value of ΔE_c is:

$$\Delta E_c = -\pi R_c^2 h \Delta \bar{g} + 2\pi R_c h \gamma = -\Delta \bar{g} V_c + R_c \gamma A_c = (aR_c/2)kT = \pi h R_c^2 \Delta \bar{g} = V_c \Delta g. \tag{15}$$

According to Equation (11), the nucleation and sequential growth rate is:

$$\dot{V} = 2\pi h R_c n_c \cdot \dot{R} \ (= 2\pi h R_c n_0 \exp(-(V_c \Delta \bar{g} + \Delta E_{t,d})/kT) \cdot \dot{R}). \tag{16}$$

This equation will be discussed in Section 5.

4. Equilibrium condition of homogeneous and heterogeneous embryos

4.1. Homogeneous nucleation

The derivation of Section 3 can be repeated for homogeneous nucleation. Analogous to Equations (11) and (12) of Section 3 is for spherical embryos:

$$dV/dt = \dot{V} = d(n(4/3)\pi R^3)/dt = \big((\partial n/\partial R)(4/3)\pi R^3 + n4\pi R^2\big) \cdot \dot{R} \tag{17}$$

$$\dot{v} = ((\partial \ln n/\partial R)(4/3)\pi R^3 + 4\pi R^2) \cdot \dot{R} = ((\partial \ln n/\partial R) + A_e/V_e)(4/3)\pi R^3 \cdot \dot{R} \tag{18}$$

For $\partial \ln n/\partial R = 0$ at $R = R_c$ is now required: $\partial \ln n/\partial R = (-a + aR/R_c)R$, to have a negative slope for decreasing n at increasing R (for $R \leq R_c$) and to have an exponential third degree term in R, necessary for the possibility of the expression in a specific free energy value. Integrated is:

$$n = n_c \exp(-aR^2/2 + aR^3/(3R_c) - \Delta E_{t,d}/kT) = n_c \exp\big((-\Delta E - \Delta E_{t,d})/kT\big) \tag{19}$$
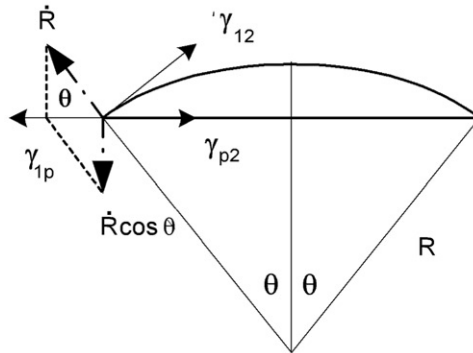
Figure 4. Spherical cap.

and: $aR^3/3R_c = ((4/3)\pi R^3 \Delta\bar{g})/kT$, or: $a = 4\pi R_c \Delta\bar{g}/kT$ and $-aR^2/2 = -4\pi R^2(R_c\Delta\bar{g}/2)$. The classical value γ now is: $\gamma = R_c\Delta\bar{g}/2$ as also found in Section 2. The critical value for

$$R = R_c \text{ is } \Delta E_c/kT = aR_c^2/6 = (2/3)\pi R_c^3\Delta\bar{g}/kT \left(\text{or} := 16\pi\gamma^3/(3(\Delta g)^2/kT)\right). \quad (20)$$

4.2. *Heterogeneous nucleation*

The formation of a critical embryo on a foreign surface will show the minimum A_e/V_e shape by its form of a spherical cap (Figure 4). According to the classical model, the free energy of formation of this heterogeneous embryo is:

$$\Delta E = \Delta g(\pi/3)(2 - 3\cos\theta + \cos^3\theta)R^3 + 2\pi(1 - \cos\theta)R^2\gamma_{1,2} + \pi(R\sin\theta)^2(\gamma_{2p} - \gamma_{1p}) \quad (21)$$

where surface energies are regarded to be identical to surface stresses (Figure 4). Resolving these surface stresses into horizontal components: $\gamma_{1p} = \gamma_{2p} + \gamma_{12}\cos\theta$, the critical value: $\Delta E_c = 4\pi\gamma_{1,2}^3(2 - 3\cos\theta + \cos^3\theta)/(3\Delta g^2)$ is found when also $R_c = 2\gamma/\Delta\bar{g}$ is applied. This is a factor $((2 - 3\cos\theta + \cos^3\theta)/4)$ times the homogeneous value of Equation (3). However the model of surface stresses, equal to the surface free energies, being in equilibrium at the intersects, does not apply for solids and should be replaced by continuity conditions of the growth rate. Because the rates $\dot{R}$ are perpendicular to the surfaces (Figure 4), because of the radial growth, they are also perpendicular to the assumed fictive surface stresses in these planes and the same expressions occur by the condition of continuity of the rates (the equilibrium of rates) as would occur by the equilibrium condition of the fictive surface stresses. The rate of growth of the spherical cap volume is:

$$\mathrm{d}\left((\pi/3)(2 - 3\cos\theta + \cos^3\theta)R^3\right)/\mathrm{d}R = \pi(2 - 3\cos\theta + \cos^3\theta)R^2\dot{R}. \quad (22)$$

This should be equal to the growth rates at the two surfaces.

The growth rate at the spherical surface is: $2\pi(1 - \cos\theta)R^2\dot{R}$.

The growth rate at the flat circular plane is: $-\pi(R\sin\theta)^2\dot{R}\cos\theta$ (where: $\dot{R}_{\text{circle}} = \dot{R}\cos\theta$).

Summing up, in total at the planes: $\pi R^2 \dot{R}(2 - 3\cos\theta + \cos^3\theta)$ due to the continuity condition of the rates in accordance with Equation (22). There thus is no need to introduce surface energies and γ- stresses and the continuity conditions are automatically fulfilled, as shown by the derivation according to Section 3.

According to Section 3 the following equation is analogous to Equation (11):

$$\dot{V} = \mathrm{d}(n(4\pi R^3/3)((2 - 3\cos\theta + \cos^3\theta)/4))/\mathrm{d}R \tag{23}$$

leading to the same equations as in Section 4.1 above for homogeneous nucleation when everywhere 'π' is replaced by '$\pi(2 - 3\cos\theta + \cos^3\theta)/4$'.

The critical value of ΔE then is:

$$\Delta E_c = \left((\pi/6)(2 - 3\cos\theta + \cos^3\theta)R_c^3\right)\Delta\bar{g} \tag{24}$$

which is identical to the classical value when: $R_c = 2\gamma/\Delta\bar{g}$ is substituted.

5. Estimation of the nucleation equation

The step-growth mechanism, regarded in Section 3, of the liquid–solid transformation is discussed as example. The growth rate of the step is normally sufficiently high so that each step nucleated on a surface spreads to form one molecular plane of height h in Figure 2, before the formation of a second nucleus on the surface. The growth rate then is equal to the nucleation rate times h.

According to Equation (16) this growth rate is: $\dot{V} = 2\pi h R_c n_c \dot{R}$, thus the number of reacting molecules N follows from: $\dot{N} = 2\pi h R_c n_c n \cdot \dot{R}$, where n is the molecule density of the n_c critical embryos. According to Appendix 1 this equation is:

$$\dot{N} = 2\pi h R_c n_c n \dot{R} = B N_t 2\sinh(\sigma_v\lambda/(NkT)) \approx C\exp((\sigma_v\lambda/(NkT)) \tag{25}$$

for high driving forces. Because of the first order transformation there is a discontinuity of the enthalpy, entropy and volume at the transformation temperature and the initial driving force thus has the form of:

$$\sigma_v\lambda/N_0 = \Delta H - T\Delta S = \Delta S(T_m - T) = \Delta S\Delta T, \tag{26}$$

while due to the volume change according to Appendix 3:

$$N = N_m + b_1(\sigma_{v0}\lambda/N_m)^2. \tag{27}$$

The derivation in Appendix 3 is based on high stresses and according to Equation (C5), N is proportional to the square of the initial applied stress σ_{v0} at the sites. For small driving forces when $\sigma_{v0} \to 0$, N should approach the constant equilibrium value e.g. at 'melting' N_m and thus the small term N_m has to be added to the expression of N accounting for lower stresses, which is negligible in the high stress segments nucleation of Figure 5, given by Equation (C2). Equation (25) then becomes for phase change at appropriate high driving forces:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = C\exp\left(\frac{\sigma_v\lambda}{NkT}\right) = C\exp\left(\frac{\Delta S \cdot \Delta T \cdot N_0}{kT(N_m + b_1(\Delta S)^2(\Delta T)^2)}\right) = C\exp\left(\frac{D'}{\frac{a_1}{\Delta T} + \Delta T}\right), \tag{28}$$

where $D' = \Delta S N_0/(kTb_1\Delta S^2)$ and $a_1 = N_m/(b_1\Delta S^2)$.
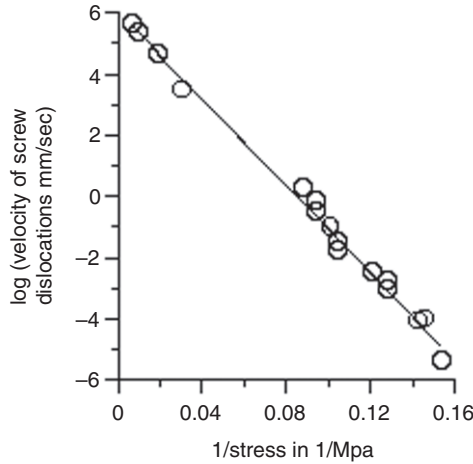
Figure 5. Dislocation velocity in LiF – Equation (C2).

Equation (28) is given for ice in Figure 3 by the dashed line together with Equation (9) of the classical nucleation model, given by the straight solid line.

By much higher stress due to much higher undercooling for homogeneous nucleation, σ_v of Equation (28) may become the maximal 'flow' stress at that temperature and Equation (28) turns approximately to Equation (6):

$$\dot{N} = C_1 \exp(\sigma_f \lambda / NkT) = C_1 \exp(C_2/(N_m + b_1(\Delta S)^2(\Delta T)^2)),$$

but $\dot{N}$ is finite, $= C_1 \exp(C_2/N_m)$, when $\Delta T = 0$. This high internal stress also may apply for heterogeneous nucleation and is e.g. found for crystallization of a metallic glass [5] showing the activation energy for viscous flow, in stead of the much lower activation energy for diffusion.

For low driving forces of liquids near melting, the sinh-equation of Equation (25) applies. Thus:

$$\dot{N} = C' \sinh\left(\frac{\sigma_c \lambda}{NkT}\right) \approx C' \frac{\sigma_c \lambda}{NkT} \approx \frac{D'' \Delta T}{a_1 + (\Delta T)^2} \approx D''' \Delta T$$

and $\dot{N} = 0$ when $\Delta T = 0$.

This result is generally accepted in literature and applies e.g. at diffused interphase interfaces. The high driving stress 'curve-fitting' of Equation (28) in Figure 3 follows from the mean value of the points at the ends at $1/\Delta T = 10$ and 30, and one point of the classical straight line fit, Equation (9) at $1/\Delta T = 20$. Then is: $D = 1.27$ and $a_1 = 0.0116$ or:

$$\log(\dot{N}) = \log(C) + (D'\Delta T)/(a_1' + \Delta T^2) = -9.07 + (1.27\Delta T)/(0.0116 + \Delta T^2). \qquad (29)$$

It can be seen in Figure 3 that, in this case, the classical straight line fit in $1/\Delta T$, Equation (9): $\ln(\dot{N}) = \ln(A_1) - A_2/\Delta T$, only is straight in the given range of $1/\Delta T$ between

10 and 30. Equation (9) thus is an approximation in a small range and is wrongly applied outside the range of allowable application e.g. for $\Delta T \to 0$.

The real curve, Equation (29) falls down to $1/\Delta T \approx 4$ and the curve thus explains the empirical maximum nucleation rate at some undercooling. Differentiating Equation (29) gives

$$\mathrm{d}\dot{N}/\mathrm{d}\Delta T = \dot{N} \cdot \mathrm{d}\big(D'\Delta T/(a_1' + \Delta T^2)\big)/\mathrm{d}\Delta T = 0, \text{ or } \Delta T_u^2 = a_1'. \tag{30}$$

In this case this maximal rate is at an undercooling of $\Delta T_u = \sqrt{a'} = \sqrt{0.0116} = 0.108$

Equation (30) explains the measured C-curves of the TTT-diagrams as is shown in Section 6. The fact that the data of Figure 3 follow the forward reaction Equation (30) only, shows an always high driving stress of quenching experiments. As discussed in reference [6] for glass transition, the always high driving force can be explained as follows. On sudden cooling, the shrinkage and configurational change is confined by strong side bonds. This behaves in the same way as when crossing molecules are bridging voids. The internal stress on these sites is always high and thus the crossing molecules are always under high pressure by the molecular attraction forces of the void boundaries trying to close the void. A segmental jump of the highest loaded crossing unit will unload this unit but increases the load on the adjacent crossing units causing the next one to be high loaded. The segmental jumps cause a decrease of the void volume and length and thus also a decrease of the number of jumping elements. This causes a process of decreasing sites by the decreasing void volume and stress decrease in the visco-elastic material surrounding the voids while the driving force remains high until the end, explaining that there only is a forward (and thus no backwards) reaction at nucleation.

6. Derivation of the TTT-diagram

It is standard practice to plot the rates of diffusive transformation in the form of TTT-diagrams, often called 'C-curves'

According to Equation (30) is the product N after time t_1:

$$\log(N) = \log(\dot{N} \cdot t_1) = \log(\dot{N}) + \log(t_1) = -9.07 + (1.27\Delta T)/(0.0116 + \Delta T^2) + \log(t_1). \tag{31}$$

At the maximal rate, the nose of the C-curve, $\Delta T = 0.108$, giving:

$$\log(N) = -3.17 + \log(t_1) \tag{32}$$

t_1 is the time to produce the relative amount $N/N_{\max}$ at the maximal rate: $t_1 = N_1/\dot{N}$, providing lines of e.g. 1%, 5%, 50 % etc. of transformed material.

In the same way is for time t_2 at an other temperature shift ΔT to get the same amount N:

$$\log(N) = -9.07 + (1.27\Delta T)/(0.0116 + \Delta T^2) + \log(t_2). \tag{33}$$

Subtraction of Equation (33) from Equation (32) gives:

$$\log(t_2) - \log(t_1) = \Delta \log(t) = 5.9 - (1.27\Delta T)/(0.0116 + \Delta T^2). \tag{34}$$
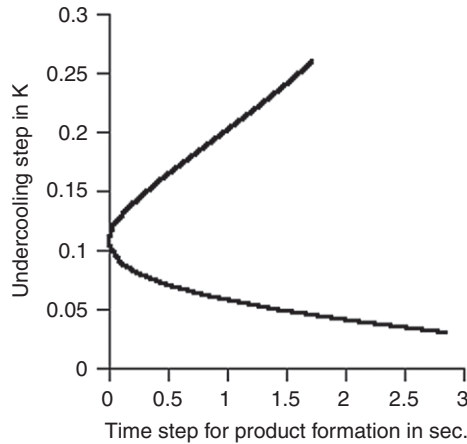
Figure 6. Reduced TTT-diagram based on data of Figure 3.

This represents the reduced curve of the TTT-diagram given in Figure 6. The curve is upside down with respect to the usually given diagrams because the temperature T is on the vertical axis and not as here the undercooling step $\Delta T = T_m - T$.

7. Some remarks regarding the practical meaning of nucleation

The formation of new phases is the result of a process of nucleation and therefore is a widely spread phenomenon in both nature and technology. Condensation and evaporation, crystal growth, electro deposition, melt crystallization, growth of thin films for microelectronics, volcano eruption, rain making and formation of e.g. glassy regions, vacancy clusters and particulate matter in space are only a few examples of nucleation processes. In practice, heterogeneous nucleation is normally involved, providing oriented and easily crystal growth at solidification or at phase change at surfaces as grain boundaries in solids.

Although a distinction is made between diffusive and displacive transformations as possible mechanisms of phase change, the nucleation equation also can be applied for the displacive mode being the reaction at the highest speed and driving force.

For practical steering of wanted results of these processes, explanation by theory is necessary. An example of application of the theory is in the Section 6 given construction of the TTT-diagram, giving the necessary information on e.g. the speed of quenching or the way of ageing to obtain a wanted result. It is not necessary to measure all points of that diagram to obtain the parameters of the equation and the equation can be applied in different circumstances to predict and explain behaviour. In the Section 5 derived equation determines a single elementary process. For more complicated behaviour is, according to the equilibrium method of [7], description of real behaviour possible by parallel acting elementary processes. This provides consistent information, better than a kinetic equation with changing parameters.

8. Conclusions

The classical nucleation theory is shown to be questionable e.g. by the apparent infinite energy and infinite fluctuation dimensions as equilibrium requirement.

Because embryo volume- and surface formation is identically coupled, the defined classical surface free energy and volume free energy must have the same temperature dependence and the assumed temperature independent surface energy can not exist.

It is shown by the general derivation of sequential growth increase that this free energy distinction is superfluous and the surface energy term thus should be omitted. This is confirmed in Section 4.2 by the proof that the separate influence of surface energy in the form of surface stresses to explain heterogeneous nucleation is not needed because the assumed equilibrium of surface stresses has to be replaced by equilibrium of rates, thus by continuity conditions, to explain heterogeneous nucleation. These continuity conditions are automatically fulfilled by the derivative of the volume in the sequential growth rate equation.

Based on sequential growth conditions, the theoretical derivation of the equilibrium concentration of the embryos depending on size is given.

It is shown in Appendix 2 that every function can be represented by the power law equation. The power is identical to the slope of the double log-plot of the power equation and is identical to the activation volume parameter of the exact kinetics equation. It is therefore possible to compare the different empirical rate equations to get information on the form of the activation volume parameter.

In Appendix 3, based on diffusion tests, the theoretical explanation is given of the different empirical equations by their different activation volume parameters, based on the derivation of the empirical power law equation in Appendix 2. Herewith the special form of the activation volume term of the driving force of nucleation is found as applied in Section 5.

It is shown in Section 5, that the special expression of the activation volume of the basic rate equation explains the data and nucleation behaviour as well for homogeneous as for heterogeneous nucleation. As discussed in Section 6, this rate equation shows the well-known increase of the rate at the increase of undercooling up to a maximum value and then a decrease of the rate at larger undercooling steps giving thus a theoretical equation and explanation of the C-shape of the TTT-diagrams.

Thus, it is shown that nucleation follows the reaction rate equation of structural change. For the common case of high internal stresses, e.g. due to quenching, the equation can be given in stresses, determinable from measurements of the rate behaviour. It is important to know that the same applies for glass transition as shown in reference [6].

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Appendix 1

Basic equation of structural change

In general the reaction rate equation for structural change can be [7]:

$$\mathrm{d}\rho/\mathrm{d}t = B \cdot \rho \cdot 2\sinh(f_a A_a \lambda/(kT)) \tag{A1}$$

where $B = \nu \exp(\Delta E_t/kT)$. This can be expressed in the concentration term:

$$\rho = N_a \lambda A_a/\lambda_1 \tag{A2}$$

where λ is the jump distance of the activated unit; A_a, the cross-section of that unit;

λ_1 the distance between the activated sites and N_a, the number of these sites per unit area. Then $N_a/\lambda_1 = N_t$ is the number of activated elements per unit volume. The work of the stress f_a on the activation unit is: $f_a A_a \lambda$.

The equivalent work by the part σ_v of the mean macro stress σ that acts at the site is σ_v times the unit area thus is:

$$\sigma_v \cdot 1 \cdot 1 \cdot \lambda = N_a f_a A_a \lambda \text{ or } f_a A_a \lambda = \sigma_v \lambda/N_a. \tag{A3}$$

Also the chemical work, expressed as an equivalent driving stress, can be added as stress to the real external stress. Equation (A1) thus becomes:

$$\mathrm{d}(N_a \lambda A_a/\lambda_1)/\mathrm{d}t = B \cdot (N_a \lambda A_a/\lambda_1) \cdot 2\sinh(\sigma_v \lambda/(N_a kT)) \tag{A4}$$

For constant λA_a at nucleation, Equation (A4) is, when $\lambda = \lambda' T$:

$$\mathrm{d}N/\mathrm{d}t = B \cdot N_t \cdot 2\sinh(\sigma_v \lambda'/(Nk)) \approx B \cdot N_t \exp(\sigma_v \lambda'/(Nk)) \tag{A5}$$

for high stresses. This structural change equation may show a long delay time and thus is able to explain transient nucleation. It also is able to explain the delay time and logarithmic time behaviour [7] of glass relaxation. Because of limited number of free spaces in solids, where molecules may jump in at diffusion, the zero order reaction occurs. The same situation follows from a high 'reactant' concentration, causing the pre-exponential value of N_t to be constant in Equation (A5).

Appendix 2

Derivation of the power law

Any function $f(x)$ always can be written in a reduced variable x/x_0

$$f(x) = f_1(x/x_0)$$

and can be given in the power of a function:

$$f(x) = f_1(x/x_0) = \left[(f_1(x/x_0))^{1/n}\right]^n$$

and expanded into the row:

$$f(x) = f(x_0) + \frac{x - x_0}{1!} \cdot f'(x_0) + \frac{(x - x_0)^2}{2!} \cdot f''(x_0) + \cdots$$

giving:

$$f(x) = \left[\{f_1(1)\}^{1/n} + \frac{x - x_0}{x_0}\frac{1}{n}\{f_1(1)\}^{1/n-1} \cdot f'(1) + \cdots\right]^n = f_1(1) \cdot \left(\frac{x}{x_0}\right)^n$$

when $(f_1(1))^{1/n} = (f_1(1))^{1/n-1}f_1'(1)/n$ or: $n = f_1'(1)/f_1(1)$, where $f_1'(1) = \partial f_1(x/x_0)/\partial(x/x_0)$ for $x = x_0$ and $f_1(1) = f(x_0)$.

Thus:

$$f(x) = f(x_0).\left(\frac{x}{x_0}\right)^n \text{ with } n = \frac{f_1'(1)}{f_1(1)} = \frac{f'(x_0)}{f(x_0)}$$

It is seen from this derivation of the power law, using only the first 2 expanded terms, that the equation only can be applied in a limited range of x around x_0.

Appendix 3

Estimation of the activation volume parameter

Because diffusion is involved, the activation energy of processes as creep, damage, self-diffusion and growth are related and correlate e.g. with the melting temperature and measurements of the dislocation mobility, by stress σ pulses, may provide information on the kinetic parameters of transformations. The possible empirical equations of [8] are:

The power law equation:

$$\dot{v} = \dot{v}_0(\sigma/\sigma_0)^m \tag{C1}$$

where $\dot{v}$ is the dislocation velocity and σ the applied stress.

The nucleation equation, based on the classical nucleation model:

$$\dot{v} = C_1 \exp(-D/\sigma)(\approx \dot{v}_0(\sigma/\sigma_0)^{D/\sigma_0}) \tag{C2}$$

This Equation (C2) of point defect drag mechanism in LiF is given in Figure 5 applying here for high stress nucleation of mobile segments by overcoming peaks of the potential energy field.

The exact theoretical equation can be given in the form:

$$\dot{v} = 2C_2 \sinh(\varphi\sigma) \approx C_2 \exp(\varphi\sigma)(\approx \dot{v}_0(\sigma/\sigma_0)^{\varphi\sigma_0}) \tag{C3}$$

for the applied higher stresses. Equation (C3) is given in Figure 7 for Ni.

The parts between the parentheses are the power law approximations of the given equations, following from Appendix 2. In a limited high stress range, fitting is possible according to all 3 Equations (C1) to (C3) at the same time, as is done for Ge in reference [8]. An extended measured stress range is necessary to see which formula applies.

The power m of Equation (C1) can be found from the slope of the double log-plot, Figure 8 (of Fe–Si), and for the other two equations in Figures 5 and 7, D and φ follow from a semi-log-plot. According to the double log-plot of the power law approximations of these equations is:

$$m = D/\sigma_0 = \varphi \cdot \sigma_0 \tag{C4}$$

giving information on the form of the parameter φ of the applying exact equation, Equation (C3).

When over a long range of stresses, Equation (C2) applies and the semi log-plot of $\log(\dot{v})$ against $1/\sigma$ shows a constant slope: $-D$, then the parameter φ of the exact equation is according
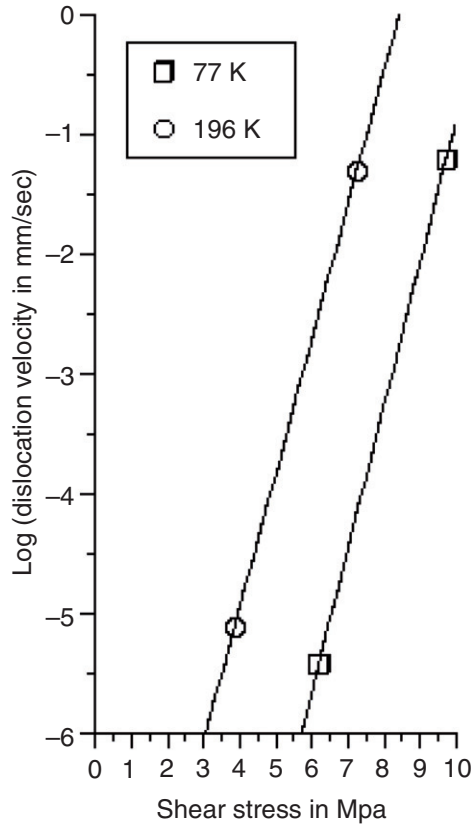
Figure 7. Dislocation velocity in Ni, Equation (C3).

to: $\varphi\sigma_0 = D/\sigma_0$, equal to $\varphi = D/\sigma_0^2$. This parameter will be shown below to be right for the nucleation mechanism. The semi log-plot of the exact equation, Equation (C3) now is for nucleation:

$$\ln(\dot{v}) = \ln(C_2) + \varphi\sigma = \ln(C_2) + D\sigma/\sigma_0^2 \tag{C5}$$

for high stresses. Because the dislocation mobility tests are done with stress pulses, long enough to get steady state velocities the applied stress σ is equal to the initial applied stress σ_0 and Equation (C5) becomes equal to Equation (C2) which thus is the equation of the collection of all different pulse tests with different values of σ_0. The value $D\sigma/\sigma_0^2$ becomes $D\sigma_0/\sigma_0^2 = D/\sigma_0$ in the positive σ-direction. Because $\partial\sigma/(\sigma_0)^2 = -\partial(1/\sigma_0)$, this is an negative slope in the $(1/\sigma)$-direction. Equation (C5) shows that for stress relaxation (one σ_0 in one test) there will be a straight-line on the $\ln(\dot{v}) - \sigma$ plot but not on the $\ln(\dot{v}) - 1/\sigma$ – plot, as is verified by experimental data of [8].

The power law behaviour, Equation (C1), when applying over a long range of stresses, also represents a mechanism with a special property of the activation volume parameter φ. The constant slope n of the double log-plot of Equation (C1) is equal to $\varphi\sigma_0$ The mechanism with this property of φ is found in many materials as in BCC, FCC and HPC metals and non-metallic crystals and also in e.g. concrete and wood. This property of φ causes the time-stress equivalence and because normally φ also is independent of the temperature, the time-temperature equivalence also applies. With the special value of $\varphi = m/\sigma_0$, Equation (C3) becomes:

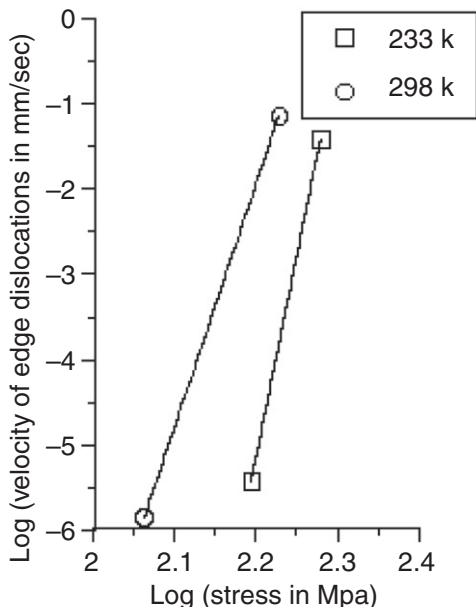$$\ln(\dot{v}) = \ln(C_2) + \varphi\sigma = \ln(C_2) + m\sigma/\sigma_0 \tag{C6}$$

Figure 8. Dislocation velocity in Fe–Si, Equation (C1).

and the semi-log-plot of $\ln(\dot{v})$ against $\sigma(=\sigma_0)$ now shows a slope of m/σ_0 which is different for every pulse test value of $\sigma(=\sigma_0)$ in the plot, thus is a curved line, as e.g. given in reference [8]. It follows also from Equation (C6) for the double log-plot:

$$\mathrm{d}\ln(\dot{v})/\mathrm{d}\ln(\sigma) = \sigma \cdot \mathrm{d}\ln(\dot{v})/\mathrm{d}\sigma = \sigma \cdot m/\sigma_0 \tag{C7}$$

This is equal to: $\sigma_0 \cdot m/\sigma_0 = m$ for the σ_0-pulse tests collection of the dislocation mobility tests, where each applied stress σ is equal to the initial applied stress σ_0. Only in this case the constant value n of the slope of the double log-plot may exist in a wide stress range, as given in reference [8]. At the same time, for the stress-relaxation tests, (which is one test with one σ_0 over many decades of time) at high stress, the straight semi log-plot: $\ln(\dot{v}) - \sigma$ – plot applies according to the exact Equation (C6), thus is fully explained here by the type of loading.

There also exists a mechanism with a constant value of φ in Equation (C3). This does not only apply for polycrystalline material like Ni, but also occurs in other materials and in wood, for instance in a species with a wavy grain.

The explanation of the form of the activation volume parameter φ follows from Appendix 3: $\sigma\varphi = \sigma\lambda/NkT = \sigma\lambda'/Nk$. Thus the power law here applies when the concentration of sites N is proportional to the initial stress σ_0: $\sigma\varphi = \sigma\lambda'/Nk = \sigma\lambda'/c\sigma_0 k = c'\sigma/\sigma_0$. For nucleation N is proportional to σ_0^2 (for high stresses), as applied in Equation (30).