Overview Annexes B "Creep, damage and transformations"

B.1.Introduction

This publication is part of compilation of work of the author to a total rigorous theory, containing the latest developments with goal of a thesis and book. The appended articles are mostly given in full as acknowledgment for the original journal publication.

The developed exact theory is given in the appended 5 publications denoted by **B**, thus: vdPut **B(1989a), B(1989b), B(2005), B(2010)** and **B(2011).** Other important derivations and applications are mentioned below and in these 5 publications. The theory in all appended publications was derived by T.A.C.M. van der Put.

The concerning empirical models, which traditionally are based on linear viscoelasticity, thus on dilute solutions models, are wrongly applied to the highly cross-linked and crystalline wood material. The lack of correlation also made it necessary to derive new theory of e.g. nucleation, **B(2011)** and glass transition **B(2010)** and to discuss transformations **B(2005)** in the light of deformation kinetics theory. The draft proposal for RILEM, to apply the wrong and impossible classical nucleation equation of solidification (needing infinite energy to obtain equilibrium) and to apply this as basic equation for all transformations (1st and 2nd order) and even for all time dependent behavior (like creep) is absurd (see **B(2005)**) and needed to be corrected by the derivation of the right exact theory, to be able to explain and predict measurements with sufficient calculable reliability. The, in general applied linear viscoelasticity does not exist and only is theoretically possible as limit behavior for very short molecules and thus surely cannot exist in structural materials like wood. The conclusions of RILEM T.C. 112, based on linear behavior, thus are invalid and dangerous because long-term extrapolations of time (and stress) dependent strength behavior then are totally wrong. Strength and time and temperature dependent behavior of materials can only be explained by the physical and chemical processes, thus by statistical mechanics (Boltzmann statistics) and reaction kinetics, and as shown, by the, in vdPut **B(1989a)** developed limit analysis equilibrium theory of deformation kinetics, aspects as diffusion and self-diffusion (creep), power law, reaction order, damage, aging, annealing, spectra, transformations, as nucleation, glass transition, and decomposition, rubber behavior, diffusion, etc., are for all processes explained by the same constitutive equation. The consequence is that the contradictory phenomenological models as the free volume model of glass-transition, the instability model of nucleation and the extrapolated flexible chain model, with non-existent linear viscoelastic relaxation spectra for rubber behavior and creep of materials, etc., have to be rejected to make reliable, (thus exact) prediction of time dependent behavior possible. Thus as consequence, time dependent behavior of wood, timber and notched wood is non-linear and the processes follow the molecular deformation kinetics equations with a correlation close to one, for all tests on the same specimen, only determined by the measuring precision of the testing equipment, (showing thus the molecular large number statistics). The variability occurs among different wood specimens. Every piece of wood thus is significantly different from the others and is an unique giant molecule. The parameters, as concentration, activation energy and volume, of the processes can (outer direct measurements) e.g. be found by creep, relaxation, recovery, long duration and complex loading-history tests at different temperatures, loading rates and moisture contents, measuring response and hysteresis and damage, by the decrease of the modulus of elasticity, etc.

Dominating during ramp loading are the viscoelastic-plastic processes. The main viscoelastic process (of side group readjustment by cooperative hydrogen bond breaking) is coupled to a damage process with a long delay time (and a very low concentration of the initial flow-unit density), which shows irreversible strain at an activation energy which is high enough for primary bond breaking. Regarding the response, these coupled processes show a constant

activation volume parameter, independent of initial stress and temperature and thus show, outer the time-temperature equivalence, also a time stress equivalence, what means that the relaxation time decreases with increasing stress and increases with decreasing stress, what explains, in the last case, the quasi permanent deformation at unloading, which only can be recovered by heating and moistening. The consequence of the decreasing relaxation time with stress increase is that the primary bond-breaking process, thus fracture, only is noticeable, within the time-scale of ramp-loading, close to the top of the loading curve. This explains that any lower bend off of the loading curve of the test is not due to fracture, and is not correlated to fracture (as also found empirically).

The following examples, only can be explained or predicted by deformation kinetics theory. The elastic full plastic description of limit analysis gives the same stress – strain relations as a parallel system of non-linear Maxwell elements (a spring with dashpot on top, see Fig. B-1).
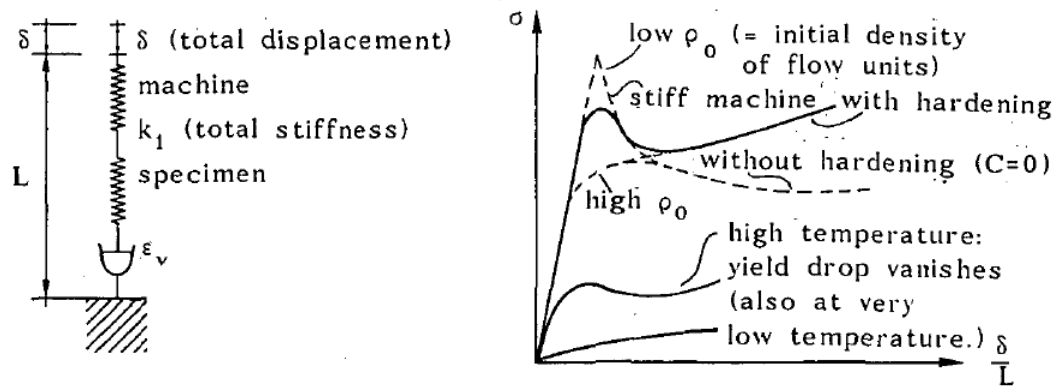

Fig. B-1. Yield drop, according to:

$$\frac{\delta}{L} = \frac{\sigma}{K_1} + \varepsilon_v \text{ or: } \dot{\delta} = L\left(\frac{\dot{\sigma}}{K_1} + \dot{\varepsilon}_v\right) \text{ or: } \dot{\varepsilon}_v = \frac{\dot{\delta}}{L} - \frac{\dot{\sigma}}{K_1} = \frac{\dot{\delta}}{L}\left(1 - \frac{L}{K_1}\frac{d\sigma}{d\delta}\right) \text{ or with } \dot{\delta} = c:$$

$$\frac{d\sigma}{d\delta} = \frac{K_1}{L} - \frac{K_1}{c}\dot{\varepsilon}_v = \frac{K_1}{L} - \frac{K_1}{c}A'T\left(\rho_0 + B'\left(\frac{\delta}{L} - \frac{\sigma}{K_1}\right)\right)\sinh\left(\varphi\sigma\left(1 - C\frac{\delta}{L} + C\frac{\sigma}{K_1}\right)\right) \quad (B-0)$$

The dashed unloading curve, in Fig. B-1, has nothing to do with softening according to the cohesive zone model. The impossible assumption of a negative E-modulus and negative dissipation is not needed. Softening and yield drop is visible impossible in a dead load test and in a constant loading rate test, (see Fig. B-2-b). In the constant strain rate test, softening is a matter of unloading (outside the fracture plane) when the rate of the flow process surmounts the rate of loading. This all follows for a positive spring constant and positive non-linear dissipation from limit analysis, by the numerical solution of the Eq.(B-0) at Fig. B-1.
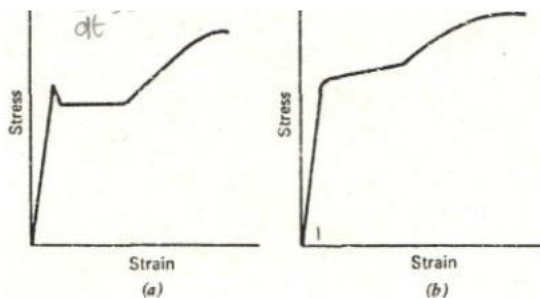

Fig. B-2. Yield behavior data (showing the work hardening of the involved processes)
(a) constant strain rate -
(b) constant loading rate test

At the first top of the loading curve of Fig. B-2a, is the rate of the crosshead of the test machine equal to the non-linear rate of flow. Then unloading occurs, because the speed of flow is higher than the crosshead speed at that stress. Next, again equal speed is possible at the lower stress as given in Fig. B-2-a. This has nothing

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to do with assumed impossible constitutive softening of the cohesive zone model. In **B(2010)** is shown that also for thermal softening as e.g. by glass transition, positive stiffness and positive dissipation is involved in the process.

B.2. Discussion of annexes B about creep, damage and transformations

As applies for all materials, time and temperature dependent behavior of wood is non-linear and has to be described by the theory of molecular deformation kinetics. The basic concept of this theory is to regard creep and plastic flow as a matter of molecular bond breaking and bond reformation in a shifted position, what is the same as to state that flow is the result of a chemical reaction like isomerization, (changing the bond structure but not the composition). Thus creep follows the chemical reaction equation of isomerization. This also applies for damage increase, when not all bonds reform. This reaction kinetics theory is always partly phenomenological, but was for the first time extended to a rigorous theory in **B(1989a)** by applying the extremum principle of limit analysis. The lower bound equilibrium method provides a rigorous prediction and explanation of time dependent behavior and of the concerning phenomenological laws. The mathematical derivation of this kinetic damage and plasticity theory is solely based on the reaction rate equations of the bond-breaking and bond-reformation processes at the deformation sites (i.e. spaces where the molecules may move into) due to the local stresses in the elastic material around these sites, according to the elastic-full plastic schematization of limit analysis. By expressing the concentration and work terms of the rate equation in the number and dimensions of the flow units, accounting for the thermodynamics of the activation energy changes, the expressions for the strain rate, fracture, hardening and delay time are directly derived without any assumptions. The reaction rate is shown in **B(2005)** to be of the first order and the activation energy and plastic work terms are constant and/or linearly dependent on temperature, moisture content and stress. The activation energy and volume provide information on the involved type of bonds and on the dimensions of the flow units. To obtain simplifications, the derivation was extended, based on series expansion of the potential energy curve, leading to a parallel acting system of symmetrical consecutive barriers with the same deformation rate of all units.
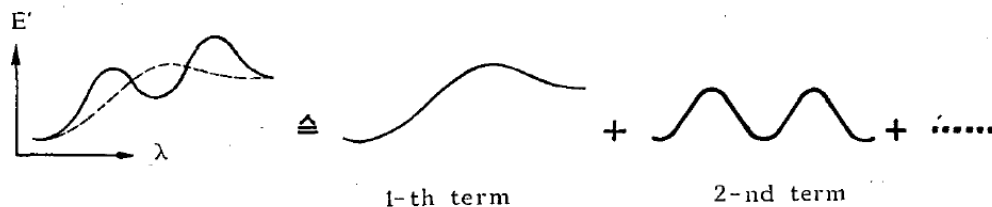

Fig. B-3. Series expansion of the activation energy barrier E'.

Because a system of the same symmetrical consecutive barriers act as one symmetrical thermally neutral barrier (thus with constant enthalpy and entropy), the total process is equivalent to a parallel system of simple, processes, in the form of Eq.(B-1). This derivation provided a proof of the generalized flow theory in **B(1989a)**, showing that the hypotheses, on which that theory was based, are consequences of this series expansion. Because the relaxation times of these parallel processes are far apart from each other, only one or two processes act and can be measured, at the same time.

The derivation of the theory is given in **B(1989)**, Section 3 and 4

In the reaction rate equation for symmetrical energy barrier expansions:

$$-\frac{d\rho}{dt} = \frac{2\rho}{t_r} \sinh\left(\frac{W}{kT}\right)$$

(B-1)

are the molecular variables replaced by the engineering values.

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The work W, by the ultimate plastic stress f on the flow unit, with area A, moving over the energy barrier over a distance λ, is (see section 3.5 of **B(1989a)**):

$$W = fA\lambda = \sigma\lambda / N \tag{B-2}$$

The concentration $\rho = NA\lambda / \lambda_1$, where N is the number of sites per unit area, and λ_1, the length of the flow segment or the distance between flow points. The part of the engineering stress per unit area σ, acting on the sites, follows from equilibrium: $\sigma \cdot 1 \cdot 1 = NfA$. Thus the reaction equation becomes:

$$-\frac{d}{dt}\left(\frac{N\lambda A}{\lambda_1}\right) = \frac{2NA\lambda}{t_r\lambda_1}\sinh\left(\frac{\sigma\lambda}{NkT}\right) \tag{B-3}$$

In this equation, A and $1/\lambda_1$ are mathematically the same variables. Thus A can be regarded constant and scratched from the equation because if there is any change possible, this will accounted by a change of λ_1. Also $1/N$ and λ are the same variables because the equation can be written:

$$\frac{d}{dt}\left(\frac{\lambda A}{N\lambda_1}\right) = \frac{2A\lambda}{Nt_r\lambda_1}\sinh\left(\frac{\sigma\lambda}{NkT}\right) , \tag{B-4}$$

and λ can be regarded constant. This equation becomes for high stresses near failure:

$$\frac{d}{dt}\left(\frac{\lambda}{N\lambda_1}\right) \approx \frac{\lambda}{Nt_r\lambda_1}\exp\left(\frac{\sigma\lambda}{NkT}\right) \tag{B-5}$$

For a high, maximal concentration of flow units, the pre-exponential factor can be regarded to change hardly or does not change as extremum principle, and the equation becomes:

$$\frac{d}{dt}\left(\frac{\lambda}{N\lambda_1}\right) = \frac{\lambda}{N_0 t_r\lambda_{10}}\exp\left(\frac{\sigma\lambda}{N_0 kT}\right) = \frac{\lambda}{N_0 t_0\lambda_{10}}\exp\left(-\frac{E}{kT}+\frac{\sigma\lambda}{N_0 kT}\right) \tag{B-6}$$

The solution of this differential equation is:

$$\frac{\lambda}{N\lambda_1} = \frac{\lambda t_f}{N_0 t_0\lambda_{10}}\exp\left(-\frac{E}{kT}+\frac{\sigma\lambda}{N_0 kT}\right)+\frac{\lambda}{N_0\lambda_{10}} , \quad \text{or:}$$
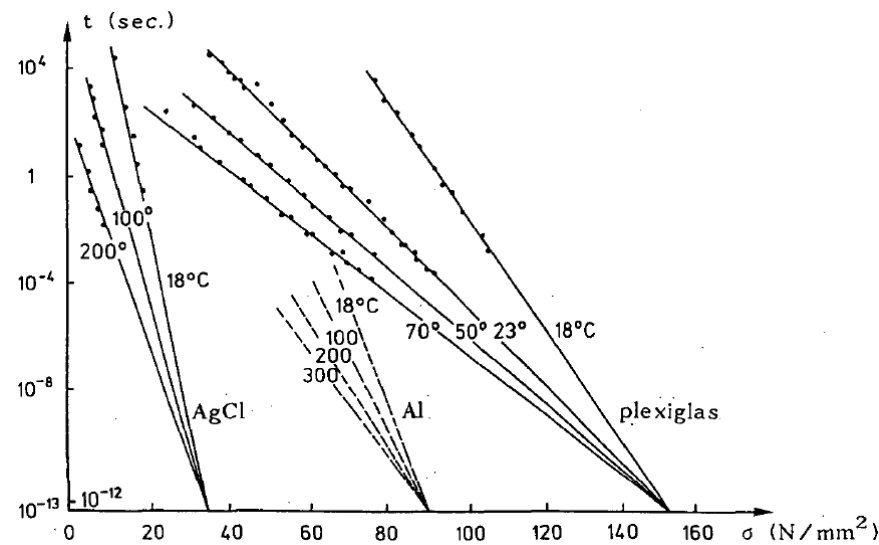

Fig. B-4. Stress and temperature dependence of the lifetime of materials.

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$$\ln\left(\frac{t_f}{t_0}\right) = \frac{E}{kT} - \frac{\sigma\lambda}{N_0 kT} + \ln\left(\frac{N_0\lambda_{10}}{N\lambda_1} - 1\right) \tag{B-7}$$
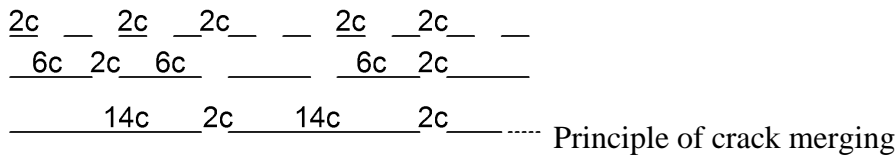
and because the lifetime should follow Eq.(B-8), according to Fig. B-4:

$$\ln\left(\frac{t_f}{t_0}\right) = \frac{E}{kT} - \frac{\sigma\lambda_0}{N_0 kT} , \tag{B-8}$$

is: $\ln\left(\dfrac{N_0\lambda_{10}}{N\lambda_1} - 1\right) = 0$, and thus is:

$$N\lambda_1 = 0.5 N_0\lambda_{10} \tag{B-9}$$

This relation, Eq.(B-9), is applied by the derivation of the small crack merging mechanism of **C(2011b)**, Section 3.6, which explains the apparent lower fracture energy for softening behavior of high loaded fracture planes. The initial small crack density is maximal with a crack distance λ_1, which is equal to the crack length. Then, as first step, two adjacent cracks merge by propagating over the distance λ_1 and the number of cracks is halved. Thus: $\lambda_1 = \lambda_{10}$ is constant and $N = 0.5 N_0$. The same applies for all next steps. The distance between two propagating adjacent crack tips is always $\lambda_1 = 2c$ and crack extension is always over a distance λ_1, halving all together the intact fracture surface.

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 2c  __   2c  _2c_  __  2c  _2c_  __
  6c  2c  6c          6c  2c
      14c      2c     14c      2c     ---- Principle of crack merging
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It thus is shown that the crack merging mechanism of **C(2011b)**, (§ 3.6) satisfies Eq.(B-9). Eq.(B-8) can be written as a normalized creep to failure strength (creep strength divided by the short - term strength):

$$\frac{\sigma}{\sigma_s} = 1 - \frac{NkT}{\sigma_s\lambda} \cdot \ln\left(\frac{t_f}{t_c}\right) \tag{B-10}$$

which is Eq.(4.5.4) of **B(1989a)**. Eq.(B-10) is one line for different wood species, moisture contents, stress states (bending, shear, compression etc.) and types of loading. This may indicate that cellulose is determining, because the structure of cellulose in the same for all
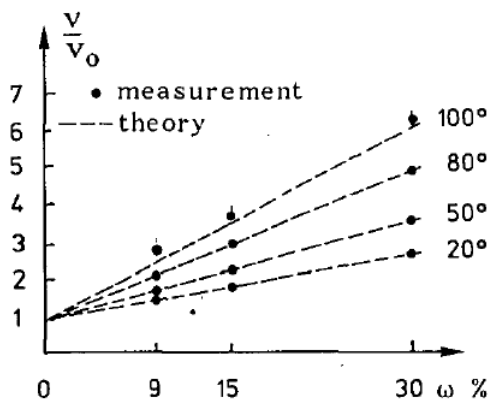

Fig. B-5. or: Fig. 4.5.2. of **(1989a B)** Activation volume (compression // test)

species. Thus $n = \sigma_s \lambda / NkT$ has to be constant, independent of the flow unit density, stress, temperature and moisture content, what explains the time-temperature and the time stress equivalence. As slope of the logarithmic creep-to-failure law eq.(B-10), is $n = 38$, when the line is scaled to the ~ 1 sec. strength, but $n = 34$ when scaled to the 5 min. strength. The value of n, following from the WLF-equation (Williams-Landel-Ferry is WLF) for glass transition, **B(2010)**, is: n = 40, equivalent to a scaling to the shortest duration strength. Thus n is essentially a structure constant and is as such unaffected by moisture content, initial stress and temperature. The in **B(1989a)**, section 6.3, given preliminary explanation of the WLF-equation for the time-temperature equivalence above glass-rubber transition, is corrected and extended by a rigorous derivation, leading, to an exact theory of glass transition in **B(2010)**. Although n is constant, this does not apply for the activation volume $V = \lambda / N$ which can be strongly linearly dependent of the moisture content and temperature (see Fig. B-5) (and thus the inverse of the strength has the same dependence). Based on this form of the activation energy, the experimental creep to failure tests at different temperatures and moisture contents could be explained as well as the straight line of the strength on log-time scale for dry wood as the curved line for saturated wood.as given by Fig. 4.5.1. of **B(1989a)**. Saturated wood shows an enthalpy of about 36 kcal/mole above a transition temperature of - 8 ^{0}C and about 30 kcal/mole below this transition temperature. Of course, dry wood doesn't show this transition to lamination of theS_2-layer.

The value of n is probably the result of two main processes. Reported are values of $n \approx 62$, for controlled crack growth tests, to $n \approx 65$, for constant strain rate tests, indicating 2 adjacent cellobiose units as fracture site and $n \approx 30$ in constant load, creep to failure tests, based on 1 cellobiose unit of the first dominating process.

Analyzing the creep values at not too high stress , the existence of two parallel barriers was clearly demonstrated. The quick process had a high internal stress (forward activation only) and an activation energy of approximately 50 kcal/mole which is high enough for primary C-O-bond or C-C-bond rupture. The fact that this process is quick, despite the high activation energy, shows that the internal stress is high, as occurs at initial crack extension to its equilibrium length at that stress, providing the sites for following crack extension. However, this primary bond breaking process is of minor importance in the ramp loading tests of fracture mechanics. Comparable (high enthalpy) processes only dominate at high stress levels, e.g. in controlled crack growth tests. The slower process was approximately symmetrical and had an activation energy of about 21 kcal/mole. The quick process, that was determining in the first stage of the loading may probably be associated with the first determining crack propagation process with n ≈ 62 and the second process may be associated with the slower process with $n \approx 30$. The activation energy of this slow process is comparable with other values mentioned in literature where from creep tests at different temperatures for bending: H' = 22 kcal/mole to 24.4 kcal/mole, depending on the temperature range, have been found. From normal-to-grain relaxation tests 23 kcal/mole was reported for wet beech wood. This energy can be regarded to be the energy of cooperative hydrogen bond breaking.

Based upon these results, also an explanation of the different power models (of the stress and of the time) is possible, giving the physical meaning of the applied exponents and constants. It further is shown that the Andrade-type power equation is equivalent to the theoretical logarithmic creep behavior. The inverse of the power parameter of e.g. the Andrade or Clouser equations is equal to the external work parameter of the activation energy ($n = \sigma V / RT = \sigma \varphi = \sigma \lambda / NRT$) and has same meaning as the exponent n of the empirical power law equation for the creep rate and the exponent of the Forintek damage model. Further is also 1/n the slope of the normalized logarithmic creep and relaxation lines and of the logarithmic time to failure law of the creep strength or long duration strength. The value of n is e.g. in the Clouser equation $n \approx 33$. In the Forintek equation is $n = 34$.

It is further shown in **B(1989a)**, that a relaxation or retardation spectrum does not exist. By the special property of the activation volume parameter $\varphi / v = c$ (constant), is a single nonlinear process sufficient to explain the measured, broad, nearly flat mechanical relaxation spectra of glasses and crystalline polymers **B(2005)** and an outline of the whole apparent relaxation spectrum of wood can be explained by two processes instead of the assumed infinite number of linear processes. Also the loss-spectrum by forced vibrations and the fatigue behavior can be explained by one non-linear process and the behavior at long term loading and at fatigue loading is coupled by the same mechanism. Thus it will be possible to use fatigue tests in order to predict the long term strength.

The solutions of the model equations for transient processes are given for different loading histories and it is shown that the model is able to explain the applied logarithmic and power relations of the phenomenological laws but that the theory, (as exact theory) has to be applied to be able to guarantee a right calculable reliability.

Several processes are acting in wood at loading. For the main damage process the stress independent part of the activation enthalpy and entropy are constant, independent of the temperature and the moisture content. The work term n of this process is about 30 to 40, depending on the scaling strength ($n = (\sigma V)/(kT) = \sigma \lambda / NkT \approx K_2 \varphi \varepsilon_0$). The activation enthalpy is about 36 kcal/mol. Probably this is the result of a cooperative reaction of a primary and a side bond rupture process. The primary bond breaking process (with $n \approx 60$) dominates at controlled crack growth tests.

The features of the main creep process are different. The work term n or $\varphi \varepsilon_0$ is constant independent of the temperature and highest initial strain ε_0 ever, at constant moisture content. The enthalpy is about H' = 24 kcal/mol and n is about 36 for dry wood. The flow unit density N is proportional to the moisture content (and is constant at zero content). Coupled to this mechanism is another mechanism with a lower value of $\varphi \varepsilon_0$ and a long delay time (of flow unit multiplication) that occurs after some critical viscoelastic strain (0.4%) of the first mechanism and this first mechanism creates the flow units for the second mechanism. The additional creep strain of this second mechanism is irreversible. The coupling follows from the same time-temperature and time stress equivalence. Besides these dominating mechanisms, that are related to the cellulose and hemicellulose, there is a small mechanism with a low value of $\sigma \varphi$ (n = 1) and a short relaxation time that is only noticeable at very high loading rates. For dense species with a high lignin content, a flow unit multiplication mechanism dominates with a stress independent relaxation time. It can be deduced that for this mechanism $\varphi \varepsilon_v$ and thus $\varphi \varepsilon^2$ is constant. Th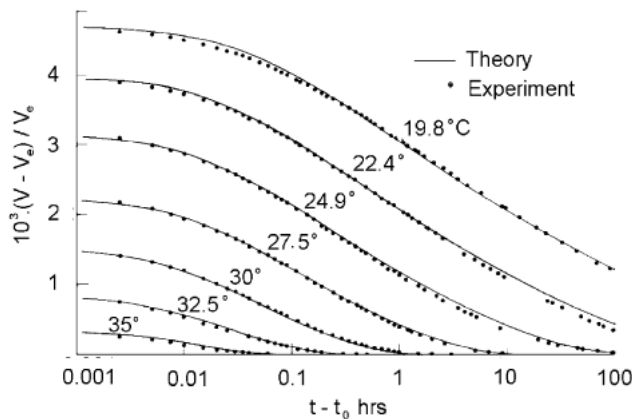us the density of the flow units is proportional to the plastic strain. The constancy of $\varphi \varepsilon_v$ applies only for constant temperature and moisture content. Probably $1 / \varphi \varepsilon_v$ is linear dependent on ω and T. This process causes rotation of the relaxation lines at short times in proportion of the strain. When this process is finished ($t = t_m$) , it can be seen from eq.(5.5.10) of **B(1989a),** that the relaxation lines for longer times ($t > t_m$), are shifted vertically according to: $\sigma_1 / \sigma_2 = \varepsilon_{01} / \varepsilon_{02}$.

Fig. B-6 Sudden cooling contraction of glucose (test-points and theory: Eq. (33))

Also possible is a mechanism with constant φ and a reliable creep model has to contain all of these processes as parallel acting mechanisms.

A special interaction of 2 processes gives the explanation of the mechano-sorptive effect in **B(1989b)**. Absorption of water in wood causes swelling up to a moisture content of about 28%. Swelling of the secondary wall is much greater than swelling of the middle lamella. With respect to the stress-less volume increase, there thus are layers with slip at desorption and layers with slip at adsorption in the mechano-sorptive model. The high restraints for swelling and shrinkage will cause "flow" in the gel-like matrix. This flow is directed if a specimen is maintained under stress during a change in moisture content. The moisture movement through the wood involves breaking of stressed hydrogen bonds and reformation of these bonds in a shifted position by, at the same time, swelling and shrinking of adjacent layers, causing, as explained by the model, the large creep deformation at desorption in the first moisture cycle. At absorption there is a partial recovery of this deformation by the reversed behavior.

B.2. Transformations of wood and wood-like polymers

In **B(2005)**, the applied, untenable phenomenological models of transformations are discussed and replaced by the exact theory of reaction kinetics, to make a real explanation and prediction of behavior possible. This leads to a new theory of solidification, nucleation, glass transition, annealing, diffusion, Rouse and Zimm and other spectra, power law, reaction order, aging and decomposition, etc. Parts of this theory are published in different articles, as
1) "Theoretical derivation of the WLF- and annealing equations" **B(2010)**, where, based on the deformation kinetics approach and the special property the activation volume term, the theoretical derivation is given of the empirical WLF-equation of the time–temperature equivalence. The same is done for annealing at glass transition. The derivation provides a general theory for any loading history and replaces the inconsistent free volume model.
2) "A new theory of nucleation" **B(2011)**. where the classical nucleation and growth model is shown to be impossible. Therefore a new theory is derived, showing that nucleation is just a common example of the kinetic theory of transport processes, with a special property of the activation volume parameter, following from the equilibrium theory of deformation kinetics. The special properties of the activation volume is determining in all processes and need to be studied further. For instance is φ / ν constant at forced vibration, showing the number of sites N, to be proportional to the frequency time, causing a perfect flat relaxation time spectrum.
3) The mechano-sorptive effect, discussed in **B(1989a)**, **B(1989b)** which occurs in wood by moisture cycling, can be explained by deformation kinetics, as a bond breaking process of secondary bonds, causing internal shifts of adjacent layers with respect to each other, due to sorption. It was for the first time possible to describe the mechano-sorptive effect by the kinetic theory, and a preliminary indication is given of dominant model parameters when external loads produce a tensile or compressive stress in the fibers. The theory predicts that for large dimensions of the test specimens, there will be only a small force exchange between the layers, and the sorption effect is of minor importance. In any case the theory makes it possible to account for it and to design for it.

It is shown in **B(2005)**, that the wood-polymer shows no first order transformations. Examples of first order transformations of wood-material (components) are the changes as: melting, crystallization, depolymerization, degradation, dehydration and some types of plasticize and hardening. Transformations of wood components mentioned in literature are based on highly degraded material. Wood does not follow these transformations of the degraded components. Wood is not a heterogeneous composite and will not show transformations of the components, but is a homogeneous composite and shows one

intermediate transition point as copolymer depending on the composition. For the structural use of wood, transformations play no role. At common temperatures, loading levels and moisture contents there is no indication of any transformation and there thus also is no aging or change of crystallinity, chemical changes, or change of concentration of flow units (determining creep etc.) during very long times. Long term loaded wood (Hinoki) of old Japanes temples, did show an increase of strength during the first 400 years and then a slow decrease during the next 1000 years, due to a process of increase of crystallinity and a slower process of decomposition of cellulose. This follows from a piezoelectric shear modulus that shows the same behavior and from the X-ray diffraction patterns being sharper for 350 years than for 8 years old wood and being diffuse for 1400 years old wood, indicating the decrease of crystallinity although the strength and stiffness still was higher than for 8 years old wood. Aging of wood at normal conditions and low stresses thus is extremely slow and the changes at common times are not noticeable. If not neglected, a net strength increase, at low or zero stresses, could be accounted for of about 1 % in 10 years (during the first 400 years) at common temperatures (indicating the common creep value of the activation volume parameter of this kinetic process of n = 33). The (degraded) composite wood shows a higher crystalline melting point than is mentioned for the components. Dynamic DTA and DSC tests did show the endothermic melting peak to be at about 380 ^{0}C, and is higher crystalline than is mentioned for the components, occurring at the high temperatures where also depolymerization and degradation occurs (failure of the chain oxygen linkages). Decomposition thus is necessary to get "melting" and this "melting"-process can better be regarded as a process of endothermic decomposition. Thus first order like transformations of wood only occur at high temperatures and have a not noticeable influence on time dependent behavior at common temperatures.

Second order transformations, that may show at the transition temperature, a "step increase" of the thermal expansion coefficient, the heat capacity and the compressibility, should e.g. be detectable for wood by a fall down of the modulus of elasticity. For a real glass-rubber transition, the stiffness (or rigidity) diminishes more than 3 orders (and the strengths more than 2 orders). However wood, as highly oriented, cross-linked, filled and crystalline composite shows a leather transition and remains elastic (potential-elastic, not rubber-elastic) and only may show a reduction of the stiffness of less than one order in the stiff direction. Softening (similar to glass transition) of wood is possible at high temperatures and moisture contents (m.c.) due to high loading. The influence of m.c. is known from manufacturing densified wood. Pressing wood of 26 % m.c. at 26 ^{0} C is as easy as pressing wood of 6 % m.c. at 160 ^{0} C. By the time-stress and time-temperature equivalence, the softening temperature of wood is also strongly reduced by high loading.

A type of a leather-like transformation of wet wood is possible by a cycling load or by a cycling m.c. change. This is not a real glass-transition that only depends on its transition temperature, but may occur at any temperature and is dependent on the loading level that should be above the long-term strength. The transformation is not possible for tension in grain direction and at low moisture contents, but is measured in compression and in torsion and other loading cases in **B(1989a).**

Repeated compressional loading of small clear compression specimens (1x1x2 cm^3) at a stress level above the long-term strength did show, besides the visco-elastic strain, a strong increase of the elastic strain. Thus, a strong decrease of the modulus of elasticity. This elastic strain may become of higher order with respect to the initial strain, when pure central loading of the specimen remains possible in the test. If this is no longer possible, instantaneous compressional failure occurs. The applied stress is thus a fatigue load of the repeated central loading. The behavior is according to a damage equation or to a structural change equation and there is a delay time and an exponential increase of the elastic and viscoelastic strain.

An other way to obtain a high elastic strain is given in chapter 8 of **B(1989a).** Creep and relaxation compression tests on small clear specimens at a high stress level, with small changing moisture contents, did show, in the delay time before the high elastic state in compression, a strong increase of the activation volume and thus a much higher compressional creep and already a high elastic state for bending movement of the compression specimen. This shows that side bond breaking starts only in certain planes and changing moisture content tests should be done in combined bending and compression for parameter estimation.

For wood, the high elastic state is the result of a strength mechanism, decreasing the side bonds and it is not a glass transformation, although the deformation is partial recoverable. The real glass transformation is discussed in B(2010).

For the structural use of wood, transformations play no role. At common temperatures, loading levels and moisture contents there is no action of any transformation and there thus also is no aging effect or change of crystallinity, chemical changes, or change of concentration of flow units (determining creep). There also is no indication of second order transformations because there is no sudden change on a temperature plot of: the thermal expansion coefficient; the heat capacity; the strength and the modulus of elasticity. The only process that matters is the damage process at high loading. Stress is the only driving force then, because the chemical driving forces are negligible.

A proof is given **B(2005)** that the first order reaction always applies for all processes in wood. This lowest overall order n = 1, shows that there is one speed determining reaction and that there are no mechanisms with intermediate products. Further, the slightly lower value of the order than one, at higher concentrations, indicates that series reactions are acting (and not concurrent reactions). Based on these results it is possible and convenient to obtain general solutions of the often complex reactions of structural changes by a sinus series expansion of the potential energy surface (as done and discussed in **B(1989a)**). Based on the symmetry conditions of the orthogonal components there is a not changing, thus steady state, intermediate concentration in the successive steps causing a behavior like one elementary symmetrical reaction for each component (see **B(1989a)**).

New theory, derived in chapter 2 of **B(2005)**, is about: nucleation and heterogeneous nucleation, (2.5), with the corrected "Tammann Hesse" equation, (2.6), and the explanation of other empirical nucleation equations, (2.5); further, about the general diffusion equation of transformations, (2.3); the reaction order, (2.4); the activation volume parameters, (2.5); the power law (2.5); and the empirical power law rate equations, (2.8). As shown in 2, the phase transformation models of liquid-like materials, with proposed linear viscoelastic behavior only may apply for idealized "Newtonian liquids", and thus certainly cannot apply for a glassy and crystalline material like wood. In general, transformations models based on a free transport of structural molecules, can not be used for wood because the (infinite) long wood-polymers only may show structural changes by secondary side bond breaking. Thus for wood only models based on the short range displacements are possible that only may give a structural change at an interface as a heterogeneous transformation. This diffusion at an interface is shown to follow the reaction equation as given in 2.3, and gets the form of the monomolecular reaction equation, eq.(2.3.10). For wood, only diffusive transformations are possible, because the martensitic transformation will not occur in wood- and wood-products. Even when a martensitic configuration may exist in wood, the elementary crystalline fibrils in wood of 3 nm are too small to be able to build up high enough internal stresses for that transformation. A derivation of a general diffusion equation for all kinds of driving forces, eq.(2.3.5), is given in 2.3, showing that Fick's first and second law are special cases.

It is shown in 2.4 that only first order reactions may occur in wood. A value of the order of one is also measured. The also measured slightly lower value than one indicates that there is

another successive reaction. This second reaction can be regarded to be of zero order, because of the nearly constant reactant.

As discussed in 2.5.1, the classical nucleation theory is not right and thus also wrong is, the thereupon based "Tammann Hesse"- equation (with its impossible negative driving force and the need of infinite energy to obtain equilibrium) that even is proposed to be the basic equation for all transformations and even for all time dependent behavior (including creep). The nucleation theory derived in 2.5.2, is further extended and corrected in **B(2011).**

The "power law" equation is derived in 2.5.3 of **B(2005)** from first 2 expanded terms of any equation. Thus, every equation can be written as power law-equation. By using the power law form, it is possible to compare and explain the power value n of eq.(2.5.3.4) of the different empirical equations with those of the exact equation, eq.(2.5.3.6), $n = \varphi\tau_0$ to get information on this activation volume parameter. It shows e.g. the special form of $\varphi\tau_0$ for nucleation, eq.(2.5.3.8) and eq.(2.6.3), etc.

To study properties as activation energy and volume of possible transformations in materials, a study of movement the free spaces (the activated sites) is possible that is the same for self-diffusion, creep, flow, rupture and transformations as melting. Creep and stress pulse experiments show all the possible forms of the activation volume parameter (2.5). Creep tests of wood show comparable values as found for other strong structural materials.

The derivation of the empirical Johnson-Mehl-Avrami equation (see 2.7) shows that this equation only applies for the steady state stage of the transformations and thus can not apply for cross-linked polymers like wood that cannot show a steady state stage, and the equation thus is a meaningless power law equation for wood. Also the other empirical rate equations are shown, in 2.8, to be related to this equation and to apply only for Newtonian materials.

B.3. Replacement of the classical phenomenological 'Rubber Theory" by the exact equilibrium theory of molecular deformation kinetics

As shown in **B(1989a)** and **B(2005)**, the exact equilibrium theory of molecular deformation kinetics, explains precisely (correlation ~ 1) all aspects of time dependent behavior like creep, damage, transformations, etc. The same constitutive equation with the same molecular parameters as e.g. N, λ and λ_1 apply. It thus is necessary that this exact approach replaces the still generally applied linear viscoelastic rubber theory equations.

The rubber theory or theory of isolated flexible molecules applies for steady-state flow viscosity and thus not for cross-linked material, which is not able to be randomly coiled and have the Gaussian distribution of configurations and thus also cannot behave like entropy springs. Chain models thus don't apply for, and have nothing to do with (always at least cross-linked) structural materials, even not above glass transition. Further, long "isolated" chains of uncross-linked polymers also don't behave according to the free chain theory. The behavior according to the rubber theory, only approximately applies for very dilute Newtonian solutions, where isolated chains of not too short molecules (to make chain statistics and coiling possible), and of not too long molecules, (thus of low molecular weight), to prevent entanglement coupling. This applies, because rubber theory, is based on the Brownian motion of isolated flexible chains at higher temperatures above glass transition, thus deals with a very dilute solution where a separated long molecule is surrounded by solvent. As model, the motions of segment junctions of the chain are expanded into modes (like a vibrating string) and each mode corresponds to a discrete contribution to the spectrum H. To keep the series of the contributions to the response convergent, for finite results, an early, arbitrary, cut-off of the series is used. Because therefore the influence of short relaxation times is not regarded in the model, the theory is not general and only is an analog for behavior after long times (or lower frequencies). The theory thus does not deal with

higher frequencies and short-range relationships and the prediction of infinite rigidity and infinite loss at infinite high frequencies is invalid. Because of the cut-off of the series, to obtain a convergent series for finite responses, the Rouse model predicts, for all materials, a slope of the logarithmic plot of G' of 2 and a slope of 1 for the loss modulus G''. As can be seen from the data of all types of polymeric materials, this never applies. Thus, the best linear viscoelastic spectrum is not able to explain time dependent behavior. Only at a steep descent, thus in the terminal zone of uncross-linked polymers, series expansion of the non-linear process shows roughly a similar behavior as a spectrum given by such a converging series. Zimm introduced hydrodynamic interaction between the moving sub-molecules based on the calculation of steady-flow viscosity of dilute solutions. However visco-elastic data of e.g. dilute solutions of polystyrene etc., in the range and conditions where the theory should apply (e.g. in the terminal zone), don't show behavior according to the Zimm theory but do show behavior close to the Rouse equation, despite the neglect of hydrodynamic interaction and internal viscosity (= intramolecular steric effects) according to the Rouse equation. This shows that the Zimm model also is not right as also is explained by the exact kinetic theory. It is shown in **B(2005)** that the determining deformation kinetics equation of the viscoelastic behavior at longer times can be expanded into a row that is identical to the row of the Rouse equation. A still later cut-off, near equilibrium at very low stress, at the end of the relaxation process, gives the Zimm value with the slope of 2/3. The Rouse line spectrum thus is a row-expansion of one special non-linear process. This explains why there is no restriction of an application to only dilute solutions, as is the basis of the chain models. This further explains why at zero relaxation, (when there is no relaxation although the specimen is still loaded after a relaxation test), the spectrum is not present. Because the "spectrum" only exists as expanded terms of one process, it does not exist when this single process is not acting by the zero internal stress on the sites at zero relaxation.

Because for a finite, convergent result, the row according to the Rouse model needs an early cut-off of the expanded row, it therefore gives no explanation for the applied row. The explanation of the Rouse equation as an expansion of one non-linear deformation kinetics process also explains why this line spectrum (that seems physical improbable, but exists as terms of the row expansion of the exact equation) gives better results than a continuous spectrum (that does not exist). Further, it explains why the theory also can be applied to undiluted polymers, using only one friction coefficient for all types of coordinated motions. These motions, represented by the separate terms, are in fact the expanded terms of one process with one relaxation time, thus one friction coefficient.

The steeper Zimm slope, occurring at shorter times than theoretical possible, in undiluted polymers in stead of in the postulated dilute solutions, certainly can not be explained by the Zimm theory because the internal friction is of higher order with respect to a solvent friction. As shown in **B(2005)**, this slope is characteristic for the midpoint of glass-transition.

The ladder networks of Blizard and Marvin are identical with the Rouse theory with the dense line spectrum approximated by a continuous spectrum. A thorough study in the past of ladder networks with both lumped and distributed parameters, has shown that a continuous dynamic modulus function corresponds to a discontinuous relaxation spectrum with discrete lines. This confirms again the explanation of the behavior according to a row expansion of the deformation kinetics equation.

Several modifications of the series of the spectrum H (to apply it for cross-linked networks) by arbitrary characteristic modes of linked strands and networks (or series of networks) only give qualitative descriptions of the behavior at transition, e.g. with square root (Rouse; Bueche), linear, and square dependence of J'' on τ, all roughly in accordance with the range of the measurements of the different types of polymers. None of these models however is

able to explain, or to describe, the flat plateau at small times. This only is possible by reaction kinetics **B(1989a)**.

Real quantitative reasonable fits of the whole behavior are not possible by the chain and power "models". This is evident because the very long relaxation times can not be explained by extrapolation of the model to motions of large groups of strands of large dimensions, while physics (reaction kinetics) shows that the behavior is explained by the very local movement of small flow units (as side bond breaking and reformation or dislocations movements in crystals, etc.).

After a sufficient long relaxation test, a lower load level can be found of zero relaxation, showing no relaxation although the specimen still is loaded. This shows that a single non-linear process is acting because the internal stress on the sites can be zero at a lower load level. A spectrum of relaxation times thus cannot exist. This non-linear process is acting in a wide time interval of many decades (e.g. 5 to 6 decades in "crystalline" materials like metals). None of the other methods (chain models, power laws, general functions, etc.), that are based, or implicitly based, on the existence of spectra, is able to explain zero relaxation. Mostly one or two processes act in concentrated solutions and solids and the rate equation of flow is in its simplest form:

$$\sigma = \frac{\text{arcsinh}(\dot{\varepsilon}/A_1)}{\phi_1} + \frac{\text{arcsinh}(\dot{\varepsilon}/A_2)}{\phi_2} \tag{B-11}$$

For crystalline materials like metals, steady flow is also due to self-diffusion. Dislocations are held up by bad sites (impurities, alloying elements, crystal imperfections, etc), causing stress concentration in the neighborhood. This stress is relieved by diffusion of the neighbors of the bad site, because the activation heat for creep equals that for self-diffusion.

Only when no phase- or other transitions are involved, the time-temperature and time-stress equivalence may apply, as in the glass-state.

It thus clearly is shown that linear viscoelastic behavior does not exist for structural materials like wood, even not above glass transition.

To study aspects of transformations of wood, as nucleation, glass transition, annealing, etc., it is necessary to show that the exact equilibrium theory of deformation kinetics is able to explain all phenomena and provide the right, exact equations of the behavior. The first, this is discussed for nucleation:

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 also 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).

The derivation of the equilibrium concentration of the embryos, depending on size, is given, from which, 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 questionable. In Section 4 of **B(2011)**, the derivation of heterogeneous nucleation is given, 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
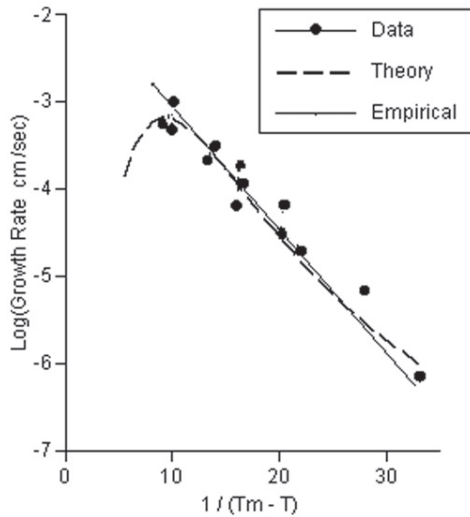
Fig. B-7. Nucleation and growth rate of ice crystals

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 this Section 5, that the special expression of the activation volume of the basic rate equation explains the data and nucleation behavior (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 explanation of the C-curves of the time-temperature-transformation diagrams (TTT-diagrams).

Regarding nucleation the following can be concluded: 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 of **B(2011)** by the proof that the separate influence ofsurface 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 of **B(2011)** 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
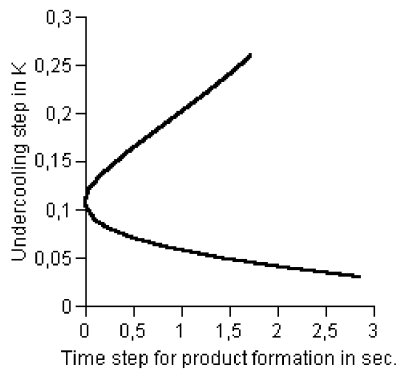

Fig. B-8. Reduced TTT-diagram based on data of Fig. B-7

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 behavior 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

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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 behavior. It is important to know that the same applies for glass transition as shown in reference **B(2010).**

Regarding glass-transition the following applies:
Based on the deformation kinetics approach, the theoretical derivation is given of the empirical WLF-equation of the time–temperature equivalence in **B(2010)**. The same is done for annealing at glass transition. The derivation provides a general theory for any loading history and replaces the inconsistent free volume model.
In general is time dependent behavior explained by the equilibrium theory of deformation kinetics of **B(1989a)** and it never was necessary to apply the phenomenological relaxation time spectra. It is, on the contrary, easy to show **B(2005)** that the row expansion of the kinetics equation gives the Rouse spectrum and with a different cut off of the series, the Zimm spectrum, explaining the success of the use of spectra. It thus follows that the apparent need of linear viscoelastic spectra indicates non-linear behavior according to deformation kinetics. This last, exact approach, also applies for glass transition and annealing and there is no need of the phenomenological free volume model and Doolittle viscosity equation giving no explanation of the WLF-equation. The explanation follows from the theoretical derivation based on the, in Appendix A of **B(2010)** discussed, deformation kinetics of structural changes and from the constitutive equations of Appendix B. Annealing had to be discussed because the determination of the constants of the WLF-equation and of the glass-transition temperature is based on annealing experiments. Two connected cases are regarded, one with the Arrhenius shift and the other with a dominating WLF-shift.
As known, viscosity curves, compliance curves, etc. measured at different temperatures may show about the same shape independent of the temperature and can be shifted along a logarithmic time or frequency axis to form one curve, predicting the behavior after long times at the lower temperature. Near glass-transition temperature, the horizontal shift factor $\ln(a_T)$
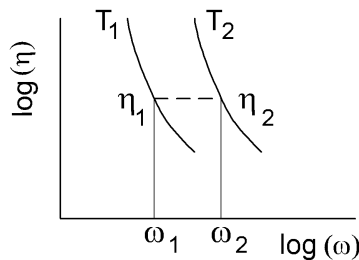

of the displacement of the curves, by temperature difference, along the log-time axis follows WLF-equation, eq.(4) of **B(2010),** applying the best for amorphous uncross-linked polymers and other super-cooled non-crystallizing liquids. According to the classical model, this shift factor is assumed to be equal to the differences in relaxation times on logarithmic scale: $\ln(a_T) = \ln(t_{r1}) - \ln(t_{r2})$,

where t_{r1} and t_{r2} are the relaxation times at temperatures T_1 and T_2 (see Fig. B-9). It further is assumed for the viscosity

Fig. B-9. Temperature shift $\quad$ η that: $\ln(\eta_1) - \ln(\eta_2) = \ln(t_{r1}) - \ln(t_{r2})$.

With the Doolittle viscosity equation:

$$\ln(\eta) = \ln(A) + B\left(v - v_f\right)/v_f = A' + Bv/v_f = A' + B/f,$$

in which $f = v_f / v$ is the free volume fraction of volume v, the shift factor a_T becomes:

$$\ln(a_T) = \ln(t_{r1}) - \ln(t_{r2}) = \ln(\eta_1) - \ln(\eta_2) =,$$

$$= B/f_1 - B/f_2 = B\frac{f_2 - f_1}{f_1 f_2} = \frac{\left(B/f_1\right)\left(T_2 - T_1\right)}{\left(f_1/\alpha\right) + \left(T_2 - T_1\right)} = \frac{c_1\left(T_2 - T_1\right)}{c_2 + \left(T_2 - T_1\right)}$$

where: $f_2 = f_1 + \alpha\left(T_2 - T_1\right)$ and α is the difference of the thermal expansion coefficients below and above the glass-transition temperature T_g, determining the increase in free volume.

Because this free volume model is a phenomenological model, there inherently are many inconsistencies. For instance, the necessity of volume changes without shear, (because of the independency of the molecular weight), while the WLF-equation also applies for shear. The value of α is an order too low for e.g. inorganic glasses, and still more for e.g. cellulose derivatives and orders to low for wood material, showing that the amount of free volume increase is not a causative parameter, but an accompanying phenomenon. The equation: $\ln(\eta_1) - \ln(\eta_2) = \ln(t_{r1}) - \ln(t_{r2})$ can not be true for a horizontal shift of the $\ln(\eta)$-plot along the frequency axis as shown in Fig. B-9, because when $\ln(\eta_1)$ at T_1, is equal to $\ln(\eta_2)$ at T_2, then also $t_{r1} = t_{r2}$, which states that there is no shifted position. Also the Doolittle equation, $\ln(\eta) = A' + Bv / v_f = A' + B / f$, can not be true for a horizontal shift, because when: $\ln(\eta_1) = \ln(\eta_2)$, then also $f_1 = f_2$, thus constant independent of temperature.

The following can be concluded regarding glass transition:

- Not the volume effect, but the structural change equation of the equilibrium theory of molecular deformation kinetics, as derived in **B(1989a)**, which is shown to explain all aspects of time dependent behavior of wood, is shown in **B(2010)** to also give the theoretical explanation of the empirical WLF-equation and of the volume change and of stress relaxation at annealing.
− The form of the WLF-equation is explained by the properties of the activation volume parameters near transition, as given by Eq. (10) of **B(2010)**.
− It is shown by Eq. (17) that the WLF-shift is accompanied by the Arrhenius shift. The right WLF-shift has to be done on an by a factor exp(H/kT) reduced curve.
− The constant value of rkg/kNg, or the proportionality of Ng (the concentration of sites) with the initial applied stress r, is a similar property of the activation volume as applies for glasses, wood, concrete and some metals B(1989a) which explains the time− stress equivalence.
− The equations show that always high internal stresses are acting
even at the end of stress relaxation, probably by the high molecular attraction forces in the voids. The decrease of stress then is due to a decrease of restrained voids.
− The WLF-shift is due to site multiplication with temperature increase near Tg.
− The WLF temperature shift applies, when the increase of specific activation volume k/kg is twice the increase of specific free volume N/Ng with temperature.
− The Arrhenius temperature shift in the transition zone applies when the increase of the specific activation volume with temperature is proportional to the increase of the specific free volume.

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