

Theoretical derivation of the WLF- and annealing equations

van der Put, Tom

DOI

[10.1016/j.jnoncrysol.2009.11.031](https://doi.org/10.1016/j.jnoncrysol.2009.11.031)

Publication date

2010

Document Version

Accepted author manuscript

Published in

Journal of Non-Crystalline Solids

Citation (APA)

van der Put, T. (2010). Theoretical derivation of the WLF- and annealing equations. *Journal of Non-Crystalline Solids*, 356(6-8), 394-399. <https://doi.org/10.1016/j.jnoncrysol.2009.11.031>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Theoretical derivation of the WLF- and annealing equations

T.A.C.M. van der Put,

TU-Delft, Civil Engineering and Geosciences, Timber Structures and wood technology,
PO Box 5048, NL-2600 GA Delft, Netherlands, *E-mail*: vanderp@xs4all.nl:

Journal of Non-Crystalline Solids 356 (2010) p 394–399

Abstract: Based on the deformation kinetics approach, 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.

PACS 64.70.Q-

1. Introduction

Time dependent behaviour is explained by the equilibrium theory of deformation kinetics (see [1]) and it never is necessary to apply the phenomenological relaxation time spectra. It is, on the contrary, easy to show (see [2]) that the row expansion of the kinetic equation gives the Rouse spectrum and e.g. the Zimm spectrum, explaining the success of the use of line spectra. The apparent need of linear viscoelastic spectra thus indicates non-linear behaviour according to deformation kinetics. This 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. This follows from the theoretical derivation based on the, in Appendix A discussed, deformation kinetics of structural changes and the constitutive equations of Appendix B. Annealing has to be discussed because the determination of the constants of the WLF-equation and of the glass transition temperature T_g is based on annealing experiments. Two connected cases are regarded, one with the Arrhenius shift and the other with a dominating WLF-shift. The results are given in the conclusions.

2. Derivation of the WLF-equation of time-temperature equivalence

As known, viscosity curves, compliance curves, etc. measured at different temperatures may show the same shape independent of the temperature and can be shifted along a logarithmic time or frequency axis to form one curve, predicting the behaviour 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), applying for amorphous uncross-linked polymers and other super-cooled non-crystallizing liquids. According to the classical model, e.g. in [3] pg.225, this shift factor is equal to the differences in relaxation times on logarithmic scale:

$$\ln(a_T) = \ln(t_{r1}) - \ln(t_{r2}) \quad (1)$$

where t_{r1} and t_{r2} are the relaxation times at temperatures T_1 and T_2 (see Fig. 1).

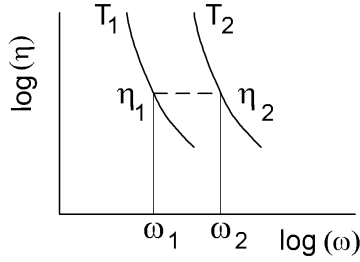


Fig. 1 – Temperature shift of the viscosity plot along the frequency axis

It is assumed for the viscosity η that:

$$\ln(\eta_1) - \ln(\eta_2) = \ln(t_{r1}) - \ln(t_{r2}) \quad (2)$$

With the Doolittle viscosity equation:

$$\ln(\eta) = \ln(A) + B(v - v_f)/v_f = A' + Bv/v_f = A' + B/f \quad (3)$$

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

$$\begin{aligned} \ln(a_T) &= \ln(t_{r1}) - \ln(t_{r2}) = \ln(\eta_1) - \ln(\eta_2) = B/f_1 - B/f_2 = \\ &= B \frac{f_2 - f_1}{f_1 f_2} = \frac{(B/f_1) \cdot (T_2 - T_1)}{(f_1/\alpha) + (T_2 - T_1)} = \frac{c_1(T_2 - T_1)}{c_2 + T_2 - T_1} \end{aligned} \quad (4)$$

where: $f_2 = f_1 + \alpha(T_2 - T_1)$ 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 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 , being an order too low for e.g. inorganic glasses, or still more for e.g. Cellulose derivatives and orders too low for wood material, shows the amount of free volume increase not to be a parameter but an accompanying phenomenon.
- Eq.(2): $\ln(t_{r1}/t_{r2}) = \ln(\eta_1/\eta_2)$ can not be true for a horizontal shift of the $\ln(\eta)$ -plot along the frequency axis as shown in Fig.(1). Because when $\ln(\eta_1)$ at T_1 is equal to $\ln(\eta_2)$ at T_2 , then also $t_{r1} = t_{r2}$ which can not be right for shifted positions.
- Also the Doolittle equation, Eq.(3), can not be applied for a horizontal shift. If $\ln(\eta_1) = \ln(\eta_2)$, then $f_1 = f_2$ (constant independent of temperature).

The Doolittle equation thus should be replaced by the empirical relation:

$$\eta = A'' \cdot \exp(B/f) \cdot \omega t_r \quad (5)$$

in order to show the shift and to be proportional to t_r according to the classical Eq.(2). Then, when $\ln(\eta_1) = \ln(\eta_2)$, Eq.(5) becomes:

$$\ln(a_T) = \ln(\omega_2) - \ln(\omega_1) = \ln(t_{r1}/t_{r2}) + B(1/f_1 - 1/f_2) \quad (6)$$

equal to Eq.(15) and Eq.(6) thus is explained by deformation kinetics providing the theoretical derivation of the WLF-equation as follows.

According to Eq.(a6) of Appendix A, the rate equation for structural change is:

$$\frac{dN}{dt} = B \cdot N \cdot 2 \sinh\left(\frac{\sigma_v \lambda'}{Nk}\right) \approx B \cdot N \exp\left(\frac{\sigma_v \lambda'}{Nk}\right) \quad (7)$$

This equation is extensively verified e.g. as damage equation for the change of bonds N , also within transition zones with changing N and λ . For instance in [1], pg. 51)

$\lambda = \lambda_0 (1 + C_0(T - T_0) \cdot \rho / \rho_0)$ applies exactly at temperature T within the temperature range of the transition for the compression strength of wood at moisture content ρ . Because the WLF-equation shows about the same activation volume parameter value:

$\sigma_v \lambda / Nk = 2.3 \cdot c_1 = 2.3 \cdot 17.44 = 40$, characteristic for self-diffusion, creep and creep to failure, the same mechanism and parameter form can be expected to apply at this “melting“ of the secondary bonds, which can be given as:

$$\lambda' = \lambda_g + \beta(T - T_g). \quad (8)$$

The same applies for the concentration N , as also applied in the empirical Eq.(4):

$$N = N_g + \alpha(T - T_g) \quad (9)$$

These linear changes with temperature T are shown in [1] to be in accordance with the thermodynamics of molecular activation. The activation volume term of Eq.(7) then is

$$\frac{\sigma \lambda'}{kN} = \frac{\sigma}{k} \cdot \frac{\lambda_g + \beta(T - T_g)}{N_g + \alpha(T - T_g)} \quad (10)$$

In this equation is N_g the site concentration at T_g , the glass transition temperature.

Because of the stress dependency of “ N ”, comparison of viscosities at different temperatures is difficult. Therefore, the shift of the curve of the apparent creep modulus (the inverse of the creep compliance) along the time axis is chosen as simple illustration of the behaviour. The rate of bond breaking and bond reformation in shifted position dN/dt is proportional to the viscous strain rate and neglecting the minor important temperature dependent pre-exponential terms, the steady creep strain rate $\dot{\varepsilon}$ is according to Eq.(7) in the form of Eq.(a5) of Appendix A:

$$\dot{\varepsilon} = A \exp(\varphi \sigma) = (\exp(\varphi \sigma)) / t_r \quad (11)$$

where t_r is the relaxation time. Integration of Eq.(11) gives: $\varepsilon = (\exp(\varphi \sigma)) \cdot t / t_r$ and the apparent creep modulus is: $E = \sigma / \varepsilon = \sigma \cdot t_r / (t \exp(\varphi \sigma))$

Thus, at the same loading σ (which should be kept the same because of the stress dependency of N), the shift of the E - plot follows from:

$$\ln(E_1) - \ln(E_2) = \ln(t_2 / t_1) + \ln(t_{r1} / t_{r2}) + \phi_2 \sigma - \phi_1 \sigma \quad (12)$$

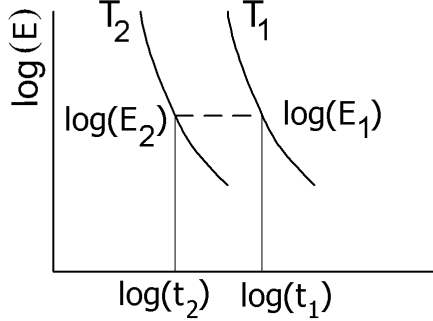


Fig. 2 – Temperature shift of the apparent creep modulus E , ($T_2 > T_1$).

For a shift of the plot along the time axis, a value $\ln(E_1)$ at temperature T_1 must be equal to $\ln(E_2)$ at temperature T_2 . Thus: $\ln(E_1) - \ln(E_2) = 0$, (see Fig. 2) or according to Eq.(12):

$$\ln(t_1 / t_2) = \ln(t_{r1} / t_{r2}) + \phi_2 \sigma - \phi_1 \sigma \quad (13)$$

In this equation is:

$$\begin{aligned} \phi_2 \sigma - \phi_1 \sigma &= \frac{\sigma \lambda_2'}{N_2 k} - \frac{\sigma \lambda_1'}{N_1 k} = \frac{\sigma}{k} \cdot \left(\frac{\lambda_g + \beta(T_2 - T_g)}{N_2} - \frac{\lambda_g + \beta(T_1 - T_g)}{N_1} \right) = \\ &= \frac{\sigma \cdot (\beta N_g - \alpha \lambda_g) \cdot (T_2 - T_1)}{k \cdot N_1 N_2} = \frac{\sigma \lambda_g}{k N_1} \cdot \frac{((\beta N_g / \alpha \lambda_g) - 1) \cdot (T_2 - T_1)}{(N_1 / \alpha) + T_2 - T_1} \end{aligned} \quad (14)$$

because: $N_2 = N_g + \alpha(T_2 - T_g) = N_g + \alpha(T_2 - T_1) + \alpha(T_1 - T_g) = N_1 + \alpha(T_2 - T_1)$.

With $n_1 = \sigma \lambda_g / k N_1$ and $m = \beta N_g / \alpha \lambda_g - 1$, Eq.(13) becomes according to Eq.(14):

$$\ln(a_T) = \ln\left(\frac{t_1}{t_2}\right) = \ln\left(\frac{t_{r1}}{t_{r2}}\right) + \frac{n_1 m \cdot (T_2 - T_1)}{(N_1 / \alpha) + (T_2 - T_1)} = \ln\left(\frac{t_{r1}}{t_{r2}}\right) + \frac{c_1(T_2 - T_1)}{c_2 + T_2 - T_1} \quad (15)$$

giving the corrected, general form of the WLF-equation. In Eq.(15) is mainly:

$$\ln\left(\frac{t_{r1}}{t_{r2}}\right) \approx \frac{H}{kT_1} - \frac{H}{kT_2} \quad (16)$$

giving the Arrhenius shift and thus a combined Arrhenius–WLF shift always applies:

$$\ln(a_T) \approx \frac{H}{kT_1} - \frac{H}{kT_2} + \frac{c_1(T_2 - T_1)}{c_2 + T_2 - T_1} \quad (17)$$

being noticeable when both amounts are comparable near transition (e.g. for methacrylate polymers, see [3]). The WLF shift thus only approximately applies when the enthalpy H is

small. The Arrhenius shift in the transition zone applies separately when $c_1 = 0$, thus when $m = 0$ and thus when: $\beta N_g = \alpha \lambda_g$, giving:

$$\frac{d\lambda \cdot N_g}{dT} = \frac{dN \cdot \lambda_g}{dT}, \quad (18)$$

Because N is proportional to the free volume Eq.(18) states that the relative increase of the activation volume with temperature is proportional to the relative increase of the free volume. This is e.g. the case for glass. When the WLF-shift applies, thus when there is a relative higher increase of specific activation volume λ / λ_g with respect to the increase of specific free volume N / N_g , this will be due to an increase of the density of active sites. If at a certain temperature step, the effective distance between the sites is halved, the number of sites is doubled and “ m ” can be expected to be:

$$m = \beta N_g / \alpha \lambda_g - 1 = \partial(\lambda / \lambda_g) / \partial(N / N_g) - 1 = 2 - 1 = 1.$$

Eq.(15) then, due to this site multiplication, also can be written as:

$$\ln(a_T) = \ln\left(\frac{t_1}{t_2}\right) = \ln\left(\frac{t_{r1}}{t_{r2}}\right) + n_1 N_1 \left(\frac{1}{N_1} - \frac{1}{N_2}\right) \quad (19)$$

explaining the extended empirical Eq.(6) when f is replaced by N .

By Eq.(14), it is shown that in the WLF-equation any reference temperature T_1 can be chosen in stead of T_g , when also N_g is replaced by N_1 . Further it follows from this derivation, that, although c_1 and c_2 of Eq.(15) are temperature dependent, depending on the choice of T_1 , the product $c_1 c_2$ is constant, temperature independent, because:

$$c_1 \cdot c_2 = m \cdot n \frac{N_1}{\alpha} = m \frac{\sigma \lambda_g}{k N_1} \cdot \frac{N_1}{\alpha} = m \frac{\sigma \lambda_g}{k \alpha} = m \frac{\sigma \lambda_g}{k N_g} \frac{N_g}{\alpha} = m \cdot n_g \frac{N_g}{\alpha} \quad (20)$$

In the equations above is: H the enthalpy and k , Boltzmann's constant. The temperature T is in K and “ N ” is the concentration of mobile segments and not the free volume concentration and thus α is not necessarily the difference of the thermal expansion coefficients below and above the transition temperature.

3. Annealing of amorphous solids

Arrhenius temperature dependence

When an amorphous material, (equilibrated far above T_g), is suddenly cooled near T_g , the liquid-like molecular adjustment to a new equilibrium becomes slow. The system is under internal stress and annealing is a process relieving the stress when the system passes to equilibrium. Accompanying this relaxation, some properties of the system (as: birefringence, specific volume, viscosity, concentration, etc.) change with time. This is discussed in Appendix B, where it shown that one and the same equation describes all these types of changes.

According to Appendix B, the rate equation of viscous flow at annealing is:

$$\dot{\varepsilon}_v = -2B\varepsilon_v \sinh(\phi K\varepsilon_v) \quad (21)$$

Performing the division $1/\sinh(x)$, or:

$$\frac{1}{e^x - e^{-x}} = e^{-x} + e^{-3x} + e^{-5x} + \dots, \text{ Eq.(21) becomes:}$$

$$d\ln(\varepsilon_v) \cdot (e^{-\phi K\varepsilon_v} + e^{-3\phi K\varepsilon_v} + e^{-5\phi K\varepsilon_v} + \dots) = -Bdt, \text{ giving as solution } (\varepsilon_{v0} > \varepsilon_v):$$

$$B \cdot t = \sum_{n=0}^{\infty} (E_1(\phi K\varepsilon_v(1+2n)) - E_1(\phi K\varepsilon_{v0}(1+2n))) \quad (22)$$

being a row solution of one process. Fitting this equation shows that there always is a high internal stress on the sites. For these high values of $\phi K\varepsilon_v$ a more simple solution is possible because Eq.(21) then becomes:

$$\frac{d\ln(\varepsilon_v)}{dt} = -Be^{\phi K\varepsilon_v} \quad (23)$$

or: $d\ln(\varepsilon_v) \cdot e^{-\phi K\varepsilon_v} = B \cdot dt$, or integrated:

$$E_1(\phi K\varepsilon_v) - E_1(\phi K\varepsilon_{v0}) = Bt \quad (24)$$

where $E_1(x)$ is the exponential integral: $E_1(x) = \int_x^{\infty} \frac{e^{-s}}{s} ds$. Thus:

$$\phi K\varepsilon_v = E_1^{-1}(E_1(\phi K\varepsilon_{v0}) + Bt) \quad (25)$$

In [4], measurements are given of the birefringence and density of a crown glass and Eq.(23) or Eq.(b5) applies exactly with a correlation close to 1 in the given temperature range between 490 to 540 °C (see Fig. 3).

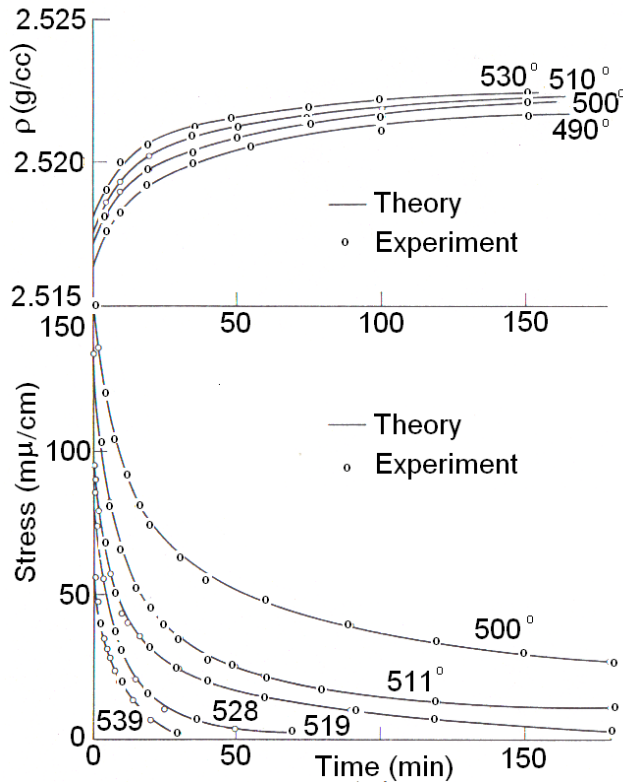


Fig.3 – Density increase and stress decrease during annealing of crown glass.

The theoretical curves follow from Eq.(24).

The test-specimens showed mutually variability of the parameters. Every specimen is an unique giant molecule. The average value of $\phi K\varepsilon_{v0} = \phi\sigma_0$, from the fit of stress relaxation and of the volume contraction data, was 4.7. However, there might be a sudden change of $\phi K\varepsilon_{v0}$, between 520 and 530 °C, from about 5 to nearly halve this value, indicating two processes acting. More data are necessary to confirm this. The variability of $\phi K\varepsilon_{v0}$ among the test-specimens is a property of glasses having a structure depending on the thermal history. This also applies for the viscosity, specific heat, specific volume, index of refraction, etc. Eq.(24) can be written for higher values of $\phi K\varepsilon_v$ as:

$$E_1(\phi K\varepsilon_v) - E_1(\phi K\varepsilon_{v0}) \approx \frac{\exp(-\phi K\varepsilon_v)}{\phi K\varepsilon_v} - \frac{\exp(-\phi K\varepsilon_{v0})}{\phi K\varepsilon_{v0}} = Bt \quad \text{or:}$$

$$\frac{\varepsilon_v}{\varepsilon_{v0}} \approx 1 - \frac{1}{\phi K\varepsilon_{v0}} \ln(1 + B\phi K\varepsilon_v t \exp(\phi K\varepsilon_{v0})), \quad (26)$$

After the delay time, the value $1 / \phi K\varepsilon_{v0}$ is the slope of the approximate straight line on $\ln(t)$ scale. This slope has to be constant independent of temperature and stress to have shifted lines along the time axis at different temperatures. The independency of stress means that in $\phi K\varepsilon_{c0} = \phi\sigma_0 = \sigma_0\lambda / NkT$, the number of sites N is proportional to the maximal initial stress σ_0 . This time-stress equivalence combined with the time temperature equivalence is mentioned in [5], pg. 94, where it is found that high strain has the same effect on aging as an increase in temperature. The time-stress equivalence is an important property of e.g. building materials, making it possible to determine the long term strength by constructing the master creep curve at constant temperature (see e.g. [1] pg.70).

From Eq.(26) follows for the shift along the time axis at different temperatures:

$$\varepsilon_{v1} / \varepsilon_{v01} - \varepsilon_{v2} / \varepsilon_{v02} = 0, \text{ that } B_1\phi K\varepsilon_{v1}t_1 = B_2\phi K\varepsilon_{v2}t_2 \text{ or:}$$

$$B_1\phi K\varepsilon_{v10}(\varepsilon_{v1} / \varepsilon_{v10})t_1 = B_2\phi K\varepsilon_{v20}(\varepsilon_{v2} / \varepsilon_{v20})t_2 \quad \text{or: } B_1t_1 = B_2t_2,$$

giving the Arrhenius shift:

$$\ln(t_1) - \ln(t_2) = \ln(B_2) - \ln(B_1) = H' / kT_1 - H' / kT_2 \quad (27)$$

WLF temperature dependence

With reference to the equilibrium values N_e and using Eq.(19), Eq.(7) becomes:

$$\frac{dN}{dt} = -B(N - N_e) \cdot \exp\left(n_e N_e \left(\frac{1}{N_e} - \frac{1}{N}\right)\right) \quad (28)$$

with: $n_e = \sigma\lambda_g / kN_e$ and $N - N_e$ as active amount of sites.

Eq.(28) can not be solved in terms of familiar functions and solutions in the form of infinite series can be obtained that can be tabulated, just like is done with $\sin(x)$, that represents an infinite series as solution of its appropriate differential equation. However, also a precise approximation is possible as follows:

Eq.(28) can be written:

$$\frac{d}{dt} \left(\frac{1}{N} \right) = B \left(\frac{1}{N_e} - \frac{1}{N} \right) \frac{N_e}{N} \exp \left(n_e N_e \left(\frac{1}{N_e} - \frac{1}{N} \right) \right) \quad (29)$$

or: $\frac{ds}{dt} = -Bs \frac{N_e}{N} \exp(s)$, where: $s = n_e N_e \left(\frac{1}{N_e} - \frac{1}{N} \right)$ or:

$$d \ln(s) \cdot \exp(-s) = -B \cdot \frac{N_e}{N} \cdot dt \quad (30)$$

At the end stage of the process $N_e / N \approx 1$ and integration of Eq.(30) then gives:

$$E_1(s) - E_1(s_0) = Bt \quad (31)$$

where $E_1(x)$ is the exponential integral.

More general the solution is: $E_1(s) - E_1(s_0) = Bt N_e / \bar{N}$, with a weighted mean value $\bar{N}$. For high values of “s” $E_1(s) = \exp(s) / s$ and the solution then becomes:

$$e^{-s} / s - e^{-s_0} / s_0 = Bt N_e / \bar{N}, \text{ being approximately:}$$

$$N e^{-s} - N_0 e^{-s_0} = B n N_e t = B' t \quad (32)$$

because for high values of s_0 and s is: $s = n_e (1 - N_e / N) = n_e (1 - N_e / \bar{N}) \approx n$, about constant and the best estimate of $\bar{N}$ is N in the first term and N_0 in the second term.

Because Eq.(31) is the solution at the safe side and Eq.(32) the solution at the unsafe side, the mean of both equations can be taken as total solution of Eq.(29):

$$N e^{-s} - N_0 e^{-s_0} + E_1(s) - E_1(s_0) = B'' t = t / t_r \quad (33)$$

The proof that this is right, follows from differentiation of Eq.(33). This gives Eq.(30) with a small negligence of $(N - N_e) / n N_e (\approx (N - N_e) / 40 N_e)$ with respect to 1. Examples of curve fitting to Eq.(33) of materials showing the WLF-shift at annealing, as glucose, Polystyrene, Polyvinyl acetate, are given in [3]. There also Fig. 4, of A Kovacs is given, showing a perfect fit by the theoretical Eq.(33).

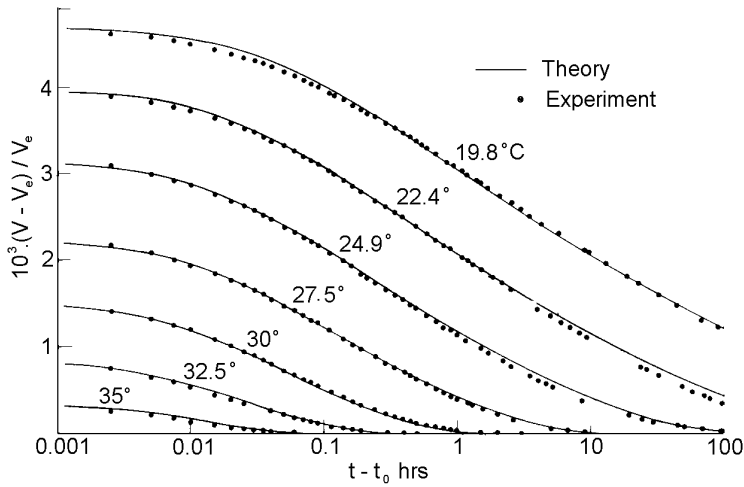


Fig. 4. Isothermal volume contraction of glucose measured after sudden cooling to the temperatures indicated from [3] (test-points and theory: Eq.(33))

4. Conclusion

- Not the volume effect, but the structural change equation (Eq.(7), Eq. (21), Eq.(28) or Eq.(b5)) of the equilibrium theory of molecular deformation kinetics, as treated in [1], which is shown to explain all aspects of time dependent behaviour of wood, is shown here to also give the theoretical explanation of the empirical WLF-equation and of the volume change and 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).
- 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 $\sigma\lambda_g / kN_g$, or the proportionality of N_g (the concentration of sites) with the initial applied stress σ , is a similar property of the activation volume as applies for glasses, wood, concrete and some metals (see [1]) 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 T_g .
- The WLF temperature shift applies, when the increase of specific activation volume λ / λ_g is twice the increase of specific free volume N / N_g 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.

Appendix A - Basic equation of structural change

As discussed in [1], the reaction rate equation for structural change:

$$d\rho / dt = B \cdot \rho \cdot 2 \sinh(f_a A_a \lambda / (kT)) \quad (a1)$$

can be expressed in the concentration term:

$$\rho = N_a \lambda A_a / \lambda_1 \quad (a2)$$

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 of the mean macro stress σ that acts at the site is σ times the unit area thus is:

$$\sigma_v \cdot 1 \cdot 1 \cdot \lambda = N_a f_a A_a \lambda \quad \text{or:} \quad f_a A_a \lambda = \sigma_v \lambda / N_a \quad (a3)$$

Also the chemical work, expressed as an equivalent chemical driving stress, can be added as stress to the external stress. Eq.(a1) thus becomes:

$$d(N_a \lambda A_a / \lambda_1) / dt = B \cdot (N_a \lambda A_a / \lambda_1) \cdot 2 \sinh(\sigma \lambda / (N_a kT)) \quad (a4)$$

$d(N_a \lambda A_a / \lambda_1) / dt$ can be the rate of increase of activation volume. If this is proportional to

the free volume, this term also gives the rate of free volume increase. $N_a \lambda A_a / \lambda_1$ also may be the mean viscous strain per unit area and Eq.(a4) then becomes:

$$\dot{\varepsilon}_v = 2B \varepsilon_v \sinh(\phi K \varepsilon_v). \text{ For pure creep, at bond breaking and bond reformation in a shifted position, the number of bonds or sites remains constant and Eq.(a4) becomes: } \dot{\varepsilon}_v = -2B \varepsilon_{v0} \sinh(\phi K \varepsilon_v) \approx -B \varepsilon_{v0} \exp(\phi K \varepsilon_v) \quad (\text{a5})$$

For a process of changing site density at annealing Eq.(a4) becomes with $\lambda = \lambda' T$ because of the entropic driving force:

$$dN / dt = B \cdot N \cdot 2 \sinh(\sigma_v \lambda' / (Nk)) \approx B \cdot N \exp(\sigma_v \lambda' / (Nk)) \quad (\text{a6})$$

This last approximation of $2 \sinh(x) \approx \exp(x)$ follows from the derivation of the WLF-equation showing always a high internal stress on the sites.

Appendix B - Basic equation of annealing relaxation

The following mechanism scheme is able to explain the measurements. At suddenly cooling, the shrinkage and configurationally change is confined by strong side bonds in the same way as crossing molecules bridging voids. It follows from the theory that 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 (free volume) as well as a decrease of the number of jumping elements. This causes a process of decreasing sites according to Eq.(a6) also by the decreasing void volume, a mean stress decrease in the visco-elastic material surrounding the voids. The rate of decrease of the void volume determines the rate of viscous displacement and thus the rate of density increase and a relief of the elastic stress in the surrounding material and a description is possible in terms of elastic and viscous strains, ε and ε_v of that material. The stress on the elastic material of the unit cross section is $\sigma - \sigma_v$ and the strain: $\varepsilon = (\sigma - \sigma_v) / E_2$, where E_2 is the modulus of elasticity of the elastic material. This strain causes a stress on the viscous sites of $\sigma_v = (\varepsilon - \varepsilon_v) E_1$ where E_1 is the equivalent modulus of elasticity of the elastic material at the site.

These constitutive equations are the same as given by the non-linear three-element analogy of Fig. 5, applied to annealing.

At a sudden cooling and no external loading, the free spring can be assumed to shorten directly what is not followed by the dashpot, and there is an internal stress

$$\sigma_v = E_1 (\varepsilon_v - \varepsilon) \quad (\text{b1})$$

This is in equilibrium with the force on the parallel spring. Thus:

$$\sigma_v = E_2 \varepsilon \quad (\text{b2})$$

and from Eq.(b1) and (b2) follows that:

$$(E_1 + E_2) \varepsilon = E_1 \varepsilon_v \quad \text{or:} \quad \sigma_v = E_2 \varepsilon = \frac{E_1 E_2}{E_1 + E_2} \varepsilon_v = K \varepsilon_v \quad (\text{b3})$$

The strain rate of the non-linear Maxwell element, for a structural change process, is:

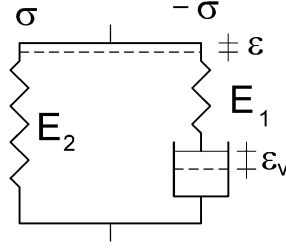


Fig. 5. Three-element model

$$\dot{\varepsilon}_v = -2B\varepsilon_v \sinh(\phi K\varepsilon_v) \approx -B\varepsilon_v \exp(\phi K\varepsilon_v) \quad (b4)$$

According to Eq.(b3), this equation also can be written in $\sigma = \sigma_v$:

$$\dot{\sigma} = -B\sigma \exp(\phi\sigma) \quad (b5)$$

giving the stress relaxation of annealing.

Eq.(b5) is the stress relaxation equation for high stresses, that does not only apply at the start, but also at the end of the relaxation process when σ approaches zero. As discussed before, this is due to the remaining high loaded units crossing the voids.

As discussed in Appendix A, a segmental jump of λ , of the bridging segments, decreases the void volume with λA_v when A_v is the surface of the bridged void. The relative decrease of the free volume then is $N_v A_v \lambda / \lambda_1$, when N_v is the number of adjacent voids per unit cross section and λ_1 the distance perpendicular. This decrease of the free volume is $N_v A_v$ times the viscous strain λ / λ_1 thus is proportional to viscous strain ε_v . In Eq.(b4), ε_v can be replaced by the free volume change being the same as the total volume change (as contraction or density increase). The same equation gives in the form of Eq.(b5) the stress relaxation. Because the birefringence (mm/mm) is proportional to the stress (for most real glasses 0.1 N/mm² produces a birefringence of 3.10^{-7}), Eq.(b5) also gives the decrease of the birefringence. Further, when the equation is written in σ / σ_0 , it also gives the change of the relaxation modulus: $(\sigma / \varepsilon_0) / (\sigma_0 / \varepsilon_0)$, or the change of the viscosity: $(\sigma / \dot{\varepsilon}_0) / (\sigma_0 / \dot{\varepsilon}_0) = \eta / \eta_0$ with time, when the relaxation modulus is measured at the different temperatures with the same ε_0 , and the viscosity with the same $\dot{\varepsilon}_0$.

References

- [1]- van der Put, TACM (1989) Deformation and damage processes in wood, Delft University Press NL.
- [2]- van der Put TACM (2003) Transformations in wood, Tech. Rep. CiTG TU-Delft
- [3]- Ferry JD, (1961) Viscoelastic properties of polymers, London, John Wiley & Sons.
- [4]- Eyring H, Hahn SJ, Ree T, (1960) Non-Newtonian Relaxation in Amorphous Solids, in: Non-Crystalline Solids, chapt. 12: ed. V.D. Frechette, Wiley, New York,
- [5]- Struik LCE (1978) Physical aging in amorphous polymers and other materials, Elsevier Scientific Publishing Company, Amsterdam.