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Time–temperature superposition principle and scaling behaviour

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The time–temperature superposition principle, frequently used to describe the mechanical and electrical relaxation behaviour of polymers, is considered within the more general concept of scaling with translation path parallel to the abscissa. The most general functions leading to scaling with translation path parallel to the horizontal axis are given. Furthermore, the meaning of the matching of the different curve segments, when the composite or master curve is constructed, is discussed. Finally, the concepts developed are applied to particular functions used for polymers and to the Williams–Landel–Ferry equation.

1. Introduction

The so called time–temperature superposition principle is widely used to extend the range of the measurements when transient or dynamic viscoelastic parameters or electrical relaxation processes are studied in polymers, as a function of time and at different temperatures [1–8]. According to this principle time and temperature are equivalent, i.e., a given property measured for short times at a given temperature is identical with one measured for longer times at a lower temperature, except that the curves are shifted on a logarithmic time axis. They can be superimposed once more by proper scale changes on this axis. Similarly, portions of the response curves can be observed at different temperatures and these curve segments can then be shifted along the log (time) axis to construct a composite curve or master curve, applicable for a given temperature, extending over many decades of time.

The shift factor for a curve segment is designated by a_T, $\log a_T$ being the horizontal displacement to allow it to join smoothly into the master curve. This is the factor by which the time scale is altered due to the difference in temperature, and is, a function of temperature. Furthermore, for all linear viscoelastic materials over a limited temperature range the horizontal shift factors are given by the empirical Williams–Landel–Ferry (WLF) equation [6]

$$\log a_T = -c_1(T - T_0)/[c_2 + (T - T_0)] \quad (1)$$

where T is the temperature, T_0 is a reference temperature and c_1, c_2 depend on T_0.

Povolo and collaborators [9–12] have analysed the scaling property observed in the experimental $\log \sigma$–$\log \dot{\varepsilon}$ creep and stress-relaxation curves in various metals and alloys. σ is the applied stress and $\dot{\varepsilon}$ the plastic strain rate. This scaling property means that it is possible to superpose by a translation ($\Delta \log \sigma$, $\Delta \log \dot{\varepsilon}$) any one of the curves onto any of the others, in such a way that the overlapping segments of each curve match within experimental error. The translation path, μ, is given by

$$\mu = \Delta \log \sigma / \Delta \log \dot{\varepsilon} = \text{constant} \quad (2)$$

The similarities between the concepts involved in the time–temperature superposition principle and the scaling property should be noticed at this point. This will be discussed later on in the paper.

Povolo [12] has established the general form of a family of curves which superimpose under a translation path along a given direction and the general conditions that a scalar field must satisfy to present a scaling behaviour. The general form of this family of curves is given by

$$g(Ax + By + Cz) = ax + by + cz + d \quad (3)$$

where g is a real function, continuous, single-valued and differentiable and A, B, C, a, b, c, d are real constants. Equation 3 can be interpreted as defining a family of curves in the (x, y)-plane, at different z-levels, or in the (x, z)-plane, at different y-levels, or in the (y, z)-plane, at different x-levels. The corresponding translation paths are given by

$$\Delta y/\Delta x = (Ac - Ca)/(Cb - Bc) \quad (4)$$

$$\Delta y/\Delta z = (Ca - Ac)/(Ab - Ba) \quad (5)$$

$$\Delta z/\Delta x = (Ab - Ba)/(Bc - Cb) \quad (6)$$

Equation 3 describes the general function leading to a scaling behaviour when curves are considered in the plane determined by two coordinate axes, parametrized in the third coordinate. Furthermore, an important point to be noticed is that a scaling behaviour in one of the planes leads to scaling in the other two planes, with different translation paths, defined by a pair of coordinate axes. Furthermore, when viewed only in one of the planes, Equations 4 to 6 also establish a relationship between the increments in the different variables.

It is the purpose of this paper to show that the time–temperature principle is a consequence of the scaling properties described by Equations 3 to 6, for the particular case where the translation path is parallel to the horizontal axis. In addition, the precise meaning of the different curve segments will be discussed and the results will be applied to different constitutive equations used for the description of viscoelastic behaviour of polymers.

2. Theory

2.1. General conditions for scaling

It is generally stated, when the curve segments are shifted along a given direction to construct the master curve, that the matching segments should join smoothly, or, as pointed out in the Introduction, that the overlapping segments of each curve match within experimental error. Clearly, this matching concept should be defined more precisely.

Fig. 1 schematically shows two curves in the (x, y)-plane, parametrized in z, related by scaling along the translation path of slope

$$\mu = \Delta y/\Delta x = \text{constant} \tag{7}$$

When curve z_1 is translated onto curve z_2, for example, i.e., when points A, A′, etc., are translated to B, B′, etc., along the translation path shown, the following conditions must be fulfilled, according to the definition of the scaling property:

(a) Points of equal derivatives should be superposed, i.e.,

$$\begin{aligned} y'_{\mathrm{A}}(x, z_1) &= y'_{\mathrm{B}}(x + \Delta x, z_2); \\ y'_{\mathrm{A'}}(x', z_1) &= y'_{\mathrm{B'}}(x' + \Delta x', z_2); \text{ etc.} \end{aligned} \tag{8}$$

where $y' = \mathrm{d}y/\mathrm{d}x$ indicates the derivative at any point.

(b) The translation path is independent of the variables, as expressed by Equation 7.

Conditions (a) and (b) define unambiguously the scaling property. Equation 3 gives the most general function satisfying these requirements. In fact, as shown by Equations 4 to 6, requirement (b) is fulfilled. The condition expressed by Equation 8 is also obeyed since by using the theorems for the derivatives of implicit functions it is easy to show that [12]

$$\partial y(x, z)/\partial x|_z = -[g'(u)A - a]/[g'(u)B - b] \tag{9}$$

where $u = Ax + By + Cz$ and $g'(u) = \mathrm{d}g/\mathrm{d}u$. Then, if $A\Delta x + B\Delta y + C\Delta z = 0$, which is one of the conditions for scaling behaviour, it is easy to show that Equation 8 is also satisfied. Analogous conditions can be obtained for the scaling in the other two planes.

The considerations made can be extended to a function of the type

$$g[Ax + By + Ch(z)] = ax + by + ch(z) + d \tag{10}$$

since z = constant implies $h(z)$ = constant, where $h(z)$ is any function of z. The conditions for scaling, in this case, are given by

$$A\Delta x + B\Delta y + C\Delta h(z) = 0 \tag{11}$$

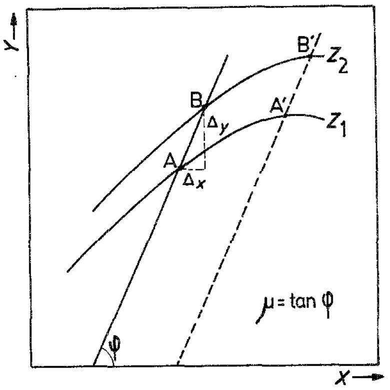

Figure 1 Two curves in the (x, y)-plane, parametrized in z, related by scaling along the translation path of slope μ. Points A, B or A′, B′, etc., have the same derivatives.

and

$$a\Delta x + b\Delta y + c\Delta h(z) = 0 \tag{12}$$

The translation path in the (x, y)-plane is unaltered. i.e., Equation 4 is valid also for this case. The other two scaling relationships are transformed to

$$\Delta y/\Delta h(z) = (Ca - Ac)/(Ab - Ba) \tag{13}$$

$$\Delta h(z)/\Delta x = (Ab - Ba)/(Bc - Cb) \tag{14}$$

It should be pointed out that similar considerations can be made for functions of the type

$$g(Ah(x) + By + Cz) = ah(x) + by + cz + d \tag{15}$$

and

$$g(Ax + Bh(y) + Cz) = ax + bh(y) + cz + d \tag{16}$$

but for scaling in the (y, z) and (x, z)-planes, respectively.

2.2. Scaling with the translation path parallel to the abscissa

In what follows and to simplify the procedure, only the (x, y)-plane will be considered, with the understanding that the extension to the other two planes is straightforward. Then, if the translation path is parallel to the x-axis, the scaling conditions for Equation 10 are reduced to

$$\Delta y/\Delta x = (Ac - Ca)/(Cb - Bc) = 0 \tag{17}$$

$$\Delta y/\Delta h(z) = (Ca - Ac)/(Ab - Ba) = 0 \tag{18}$$

$$\Delta h(z)/\Delta x = (Ab - Ba)/(Bc - Cb) \tag{19}$$

since $\Delta y = 0$. Equations 17 to 19 imply that

$$Ac - Ca = 0 \tag{20}$$

$$Ab - Ba \neq 0 \tag{21}$$

$$Cb - Bc \neq 0 \tag{22}$$

Furthermore, from Equation 20

$$a/A = c/C = k \tag{23}$$

and Equation 10 is reduced to

$$g(Ax + By + Ch(z)) = kAx + by + kCh(z) + d \tag{24}$$

which is the most general function with scaling in the (x, y)-plane, with a translation path parallel to the abscissa, i.e., with a translation path of slope $\mu = 0$.

On taking into account Equations 20 to 22 and the fact that the three variables must be involved, the following particular cases of Equation 10 also lead to scaling with $\mu = 0$:

(a)

$$A = 0;\ C = 0;\ b \neq 0;\ B \neq 0;\ c \neq 0;\ a \neq 0 \qquad (25)$$

then

$$g(By) = ax + by + ch(z) + d \qquad (26)$$

and

$$\Delta h(z)/\Delta x = -a/c \qquad (27)$$

(b)

$$A = 0;\ C = 0;\ b = 0;\ B \neq 0;\ c \neq 0;\ a \neq 0 \qquad (28)$$

then

$$g(By) = ax + ch(z) + d \qquad (29)$$

and

$$\Delta h(z)/\Delta x = -a/c \qquad (30)$$

(c)

$$a = 0;\ c = 0;\ B \neq 0;\ A \neq 0;\ b \neq 0;\ C \neq 0 \qquad (31)$$

then

$$g[Ax + By + Ch(z)] = by + d \qquad (32)$$

and

$$\Delta h(z)/\Delta x = -A/C \qquad (33)$$

(d)

$$a = 0;\ c = 0;\ B = 0;\ A \neq 0;\ b \neq 0;\ C \neq 0 \qquad (34)$$

then

$$g[Ax + Ch(z)] = by + d \qquad (35)$$

and

$$\Delta h(z)/\Delta x = -A/C \qquad (36)$$

The situation

$$A = 0;\ B = 0;\ C = 0;\ a \neq 0;\ b \neq 0;\ c \neq 0 \qquad (37)$$

leads to

$$ax + by + ch(z) = 0 \qquad (38)$$

which is a trivial case. In fact, Equation 38 leads to parallel straight lines in the (x, y)-plane, at different $h(z)$ levels, and, any translation path is possible. This is reflected by the fact that, even if Equation 20 is satisfied, Equations 21 and 22 are not fulfilled in this case.

The results given by Equations 17 to 38 are summarized in Table I. It should be pointed out that Equations 18 and 19 imply that when Equation 10 is plotted in the $[y, h(z)]$-plane, at different x levels, a scaling relationship should be observed with a translation path parallel to the $h(z)$ axis. Moreover, a scaling relationship with a translation path with a slope given by the second column of Table I should also be observed, when the function is plotted in the $[x, h(z)]$-plane, at different y levels.

In the particular case where $h(z)$ is a linear function, i.e., when

$$h(z) = \alpha + \beta z$$

then (39)

$$\Delta h(z) = \beta \Delta z$$

and the increments of x are linearly related to those of z, implying that a scaling relationship will be observed in the (x, y)-plane, at different z levels.

Finally, $\Delta h(z)$ can be expressed as

$$\begin{aligned} \Delta h(z) &= h(z + \Delta z) - h(z) \\ &= [h'(z)/1!]\Delta z + [h''(z)/2!](\Delta z)^2 \\ &\quad + [h'''(z)/3!](\Delta z)^3 + \ldots \end{aligned} \qquad (40)$$

where $h'(z)$, $h''(z)$, $h'''(z)$, etc., indicate the successive derivatives of $h(z)$ taken at the value z.

3. Applications

The superposition of the response curves, by a shifting along the log-(time) axis, to construct a composite curve or master curve according with the time–temperature superposition principle, implies, within the context of the scaling properties, that the different curves must be related by scaling with a translation path parallel to the horizontal axis. In fact, according to Bueche [2] the creep compliance, $D(t)$, when represented as

$$3vkTD(t) = \psi(t/\tau_1) \qquad (41)$$

where k is Boltzmann constant, t is the time, v is the number of network chains per unit volume, ψ is a general function and τ_1 is a function only of T, obeys the time–temperature superposition principle. This can be shown very easily by applying the scaling

TABLE I Functions leading to scaling with a translation path parallel to the abscissa axis in the (x, y)-plane, i.e., $y = 0$, when the function is plotted at different $h(z)$ levels, g is a general function and A, B, C, a, b, c, d and k are real constants. The second column gives the relationship between the increments of x and those of z.

Function	Relationship between increments
$g(Ax + By + Ch(z)) = kAx + by + kCh(z) + d$ $A \neq 0;\ C \neq 0;\ B \neq 0;\ k \neq 0$	$\Delta h(z)/\Delta x = -A/C$
$g(Ax + By + Ch(z)) = by + d$ $A \neq 0;\ C \neq 0$	$\Delta h(z)/\Delta x = -A/C$
$g(By) = ax + by + ch(z) + d$ $B \neq 0;\ a \neq 0;\ c \neq 0$	$\Delta h(z)/\Delta x = -a/c$

concepts developed, since with the change of variables

$$y = 3\nu kTD(t)$$

$$x = \ln t \qquad (42)$$

$$h(z) = \ln \tau_1(T); \quad z = T$$

Equation 41 can be written as

$$y = \psi\{\exp[x - h(z)]\} \qquad (43)$$

Equation 43 is a particular case of Equation 35 with $d = 0$, $b = 1$, $B = 0$, $A = 1$, $C = -1$ and

$$\Delta h(z)/\Delta x = \Delta \log \tau_1(T)/\Delta \log t = 1 \qquad (44)$$

A similar situation is found for expressions of the type

$$G'/T = (\varrho R/M_c)\left\{1 + \sum_{i=1}^{N-1} [\omega^2\tau_i^2/(1 + \omega^2\tau_i^2)]\right\} \qquad (45)$$

$$G''/T = (\varrho R/M_c) \sum_{i=1}^{N-1} [\omega\tau_i/(1 + \omega^2\tau_i^2)] \qquad (46)$$

where

$$\tau_i = \pi^2\tau_1/[2N \sin(i\pi/2N)]^2 \qquad (47)$$

which are frequently used to describe the relaxation behaviour of dilute polymer solutions. R is the gas constant, ϱ is the density of the material, G' and G'' are the storage and loss shear moduli, respectively, N is the number of Gaussian subchains in which the polymer molecule is divided, $\omega = 2\pi\nu$ where ν is the applied frequency and M_c is the molecular weight. The longest relaxation time τ_1 is only a function of temperature.

On taking into account Equation 47, Equations 45 and 46 can be written as

$$G'/\varrho T = (R/M_c)\left\{1 + \sum_{i=1}^{N-1} [\exp 2(\ln \nu + \ln \tau_1(T) + \ln b_i)]/[1 + \exp 2(\ln \nu + \ln \tau_1(T) + \ln b_i)]\right\} \qquad (48)$$

$$G''/\varrho T = (R/M_c)\left\{\sum_{i=1}^{N-1} [\exp(\ln \nu + \ln \tau_1(T) + \ln b_i)]/[1 + \exp 2(\ln \nu + \ln \tau_1(T) + \ln b_i)]\right\} \qquad (49)$$

where

$$b_i = \pi^2/[2N \sin(i\pi/2\nu)]^2 + 2\pi \qquad (50)$$

With the change of variables $x = \ln \nu$, $y = G'/T\varrho$ or $G''/T\varrho$, $h(z) = \ln \tau_1(T)$ and $z = T$, it is easily seen that equations 48 and 49 lead to a function of the type given by the second row of Table I, with $A = 1$, $B = 0$, $C = 1$, $b = 1$, $d = -R/M_c$ for Equation 48 and $d = 0$ for Equation 49. For both equations

$$\Delta \log \tau_1(T)/\Delta \log \nu = -1$$

Furthermore, on taking the logarithm of both sides of Equations 48 and 49 it is easily seen that a plot of $\log(G'/T\varrho)$ or $\log(G''/T\varrho)$ versus $\log \nu$ also leads to the same type of g function. Then, a representation of both functions in this way leads to scaling with a translation path parallel to the $\log \nu$ axis, or, which is equivalent, to the applicability of the time–temperature superposition principle. It should be pointed out that, according to Table I, not only a function of the type

$$\phi(T)R(t) = \psi(t/\tau(T)) \qquad (52)$$

where $\phi(T)$ is a function of temperature, $R(T)$ is some response function (creep compliance, shear modulus, etc.), leads to the applicability of the time–temperature superposition principle. In fact, Equations 41, 45 and 46 are included in this particular case. According to Table I, however, functions of the type

$$g[\phi(T)R(t)] = \phi(T)R(t)\tau(T)t \qquad (53)$$

$$g[\phi(T)R(t)t/\tau(T)] = \phi(T)R(t)t/\tau(T) \qquad (54)$$

for example, also lead to the time-temperature superposition principle when $\log[\phi(T)R(t)]$ is plotted as a function of $\log(t)$, at different temperatures.

Finally, some comments should be made to the WLF equation, i.e., to Equation 1. According to the notation used in the Theory, $\log(a_T)$ is equivalent to Δx and the scaling conditions for all the functions given in Table I imply that

$$\Delta h(z)/\Delta x = \text{constant} = K \qquad (55)$$

Equation 1 can be obtained from this condition if

$$h(z) = p + q/(r + z) \qquad (56)$$

where p, q and r are constants, independent of z. In fact,

$$\Delta h(z) = h(z + \Delta z) - h(z)$$

$$= -[q/(r + z)]\Delta z/[(r + z) + \Delta z] \qquad (57)$$

which, on taking into account Equation 55 can be written as

$$\Delta x = -[q/(r + z)K]\Delta z/[(r + z) + \Delta z] \qquad (58)$$

Equation 1 can easily be obtained by making the change of variables $\Delta x = \log(a_T)$, $z = T_0$, $\Delta z = T - T_0$ and

$$c_1(T_0) = q/K(r + T_0) \qquad (59)$$

$$c_2(T_0) = (r + T_0) \qquad (60)$$

In addition

$$c_1c_2 = q/K \qquad (61)$$

which is independent of T_0, i.e., independent from the selected reference temperature.

Equations 59 to 61 show that if the g function is known, i.e., if K is known, q and r can be obtained from the measured values of c_1 and c_2, from any reference temperature. These determine $h(z)$, except for an additive constant.

As an example, following the analysis used by Bueche [2] it can be shown that

$$\ln \tau_1 = \ln[2N^2a^2/\pi^2\phi_0\delta^2] + (\beta^*v^*/\alpha v_g)/\{[(v_{fg}/\alpha v_g) - T_g] + T\} \qquad (62)$$

where T_g is the glass transition temperature, δ is the average jump distance of the polymer segment, ϕ_0 is the pre-exponential factor for the jumping frequency, a is the average length of the free orientating segments, v^* is the critical free volume, v_g and v_{fg} are the total and the free volume, respectively, associated with each segment at the glass transition, α is the expansion coefficient for the gross liquid minus the expansion coefficient for the glass and

$$\beta^* \simeq [\ln (v^*/v_f) - 1] \qquad (63)$$

where v_f is the free volume associated with each segment, above the glass transition. Clearly, Equation 62 can be transformed to Equation 56 with $h(z) = \ln \tau_1$ and

$$p = \ln (2N^2a^2/\pi^2\phi_0\delta^2) \qquad (64)$$

$$q = \beta^*v^*/\alpha v_g \qquad (65)$$

$$r = (v_{fg}/\alpha v_g) - T_g \qquad (66)$$

Then, when the storage and loss shear moduli (Equations 48 and 49) are measured as a function of frequency $K = -1$ (Equation 51) and the constants of the WLF equation are given, in this case, by (Equations 59 to 61)

$$c_1(T_0) = -\beta^*v^*/\alpha v_g[(v_{fg}/\alpha v_g) - T_g + T_0] \qquad (67)$$

$$c_2(T_0) = (v_{fg}/\alpha v_g) - T_g + T_0 \qquad (68)$$

and

$$c_1c_2 = -\beta^*v^*/\alpha v_g \qquad (69)$$

where T_0 is a given reference temperature. Furthermore, if $T_0 = T_g$, i.e., if the reference temperature is taken as the glass transition and in the particular model of Equation 62, Equations 67 and 68 are reduced further to

$$c_1(T_g) = -\beta^*v^*/v_{fg} \qquad (70)$$

$$c_2(T_g) = v_{fg}/\alpha v_g \qquad (71)$$

Finally, it should be pointed out that a physical model is needed to determine completely the function $h(z)$, as in the case of Equation 56. When the model is not available, however, some simple particular cases can be considered, for example,

$$h(z) = a^* + b^*z^2 \qquad (71)$$

where a^* and b^* are constants. Then, from Equation 40

$$\Delta h(z) = 2b^*z(\Delta z) + b^*(\Delta z)^2 \qquad (72)$$

which, on taking into account Equation 55 can be written as

$$\Delta x/\Delta z = (2b^*/K)(z + \tfrac{1}{2}\Delta z) \qquad (73)$$

Then, if Equation 71 is obeyed, a plot of $(\Delta x/\Delta z)$ against Δz, for a given reference $z = z_0$, should lead to a straight line of slope (b^*/K) and intercept $(2b^*z_0/K)$.

4. Conclusions

General functions leading to scaling with a translation path parallel to the abscissa have been presented. Within the general formalism used, it has been shown that the time–temperature superposition principle, frequently used to describe the response functions of polymers, means that these functions must belong to the family of general functions with scaling along the abscissa.

The scaling property has been defined rigorously, to precise the meaning of the matching of the different curve segments, when the master or composite curve is constructed.

Finally, the general concepts have been applied to particular functions used in the literature to describe the mechanical response of polymers and to the Williams–Landel–Ferry equation.

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