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Mechanical vibration and shock — Characterization of the dynamic mechanical properties of visco-elastic materials —

Part 6: Time-temperature superposition

Vibrations et chocs mécaniques — Caractérisation des propriétés mécaniques dynamiques des matériaux visco-élastiques —

Partie 6: Superposition du temps et de la température

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 108, *Mechanical vibration, shock and condition monitoring*.

A list of all parts in the ISO 18437 series can be found on the ISO website.

Introduction

Visco-elastic materials are used extensively to reduce vibration amplitudes in structural systems through dissipation of energy (damping) or isolation of components and in acoustical applications that require a modification of the reflection, transmission or absorption of energy. The design, modelling and characterization of such systems often require specific dynamic mechanical properties in order to function in an optimum manner. For most visco-elastic materials, these properties depend on frequency, temperature and amplitude of applied excitation. The aim of this document is to provide details on the best way of data acquisition for subsequent processing and to provide a standard method for analysis using the time-temperature superposition principle. This document applies to the linear behaviour observed at small strain (stress) amplitudes and to thermorheologically simple materials.

This document presents a method for checking the validity of a thermorheological simplicity of a material and for identifying and eliminating questionable data. It provides minimal criteria for data acquisition to be applied in mathematical methodologies, which allow multiple data sets of dynamic visco-elastic properties measured at different temperatures to be cast into a single master curve according to the time-temperature superposition (TTS) principle. When sufficient data are obtained or available, a standard method, which uses a closed form shifting algorithm[16][17], is defined.

TTS is the most widely-used method for accelerated prediction of long-term visco-elastic behaviour of materials[13]. In the frequency domain, TTS can be used for predicting the behaviour of materials at frequencies that are experimentally not assessable.

Mechanical vibration and shock — Characterization of the dynamic mechanical properties of visco-elastic materials —

Part 6:
Time-temperature superposition

1 Scope

This document specifies a standard method for the acquisition and analysis of data obtained using the test methods found in ISO 18437-1 to ISO 18437-5, ISO 6721-4 to ISO 6721-7 and ISO 6721-12.

It is applicable to visco-elastic materials that are thermorheologically simple and that have been tested at equilibrium state for every temperature.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18437-1, *Mechanical vibration and shock — Characterization of the dynamic mechanical properties of visco-elastic materials — Part 1: Principles and guidelines*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18437-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
dynamic visco-elastic function
fundamental visco-elastic property, i.e. storage moduli and loss moduli, measured in tension, shear and compression and loss factor as functions of frequency and temperature

3.2
storage modulus
M'
real part of the complex modulus

Note 1 to entry: It is a measure of the energy stored and regained during a loading cycle.

Note 2 to entry: Storage moduli in tension, shear and compression are denoted as E', G' and K', respectively.

Note 3 to entry: It is expressed in pascals (Pa).

[SOURCE: ISO 472:2013, 2.998, modified — Notes to entry have been added.]

3.3
loss modulus
M''
imaginary part of the complex modulus

Note 1 to entry: It is a measure of the energy lost (dissipated) during a loading cycle.

Note 2 to entry: Loss moduli in tension, shear and compression are denoted as E'', G'' and K'', respectively.

Note 3 to entry: It is expressed in pascals (Pa).

[SOURCE: ISO 472:2013, 2.559, modified — Notes to entry have been added.]

3.4
loss factor
tan δ
ratio of the *loss modulus* (3.3) to the *storage modulus* (3.2) measured in tension, shear, compression or longitudinal compression

Note 1 to entry: It is given by the quotient tan $\delta = M''/M'$.

[SOURCE: ISO 472:2013, 2.557, modified — the definition has been revised.]

3.5
time-temperature superposition
TTS
principle by which, for visco-elastic materials, time and temperature are equivalent to the extent that data at one temperature can be superimposed upon data taken at different temperature merely by shifting the data curves along the logarithmic time axis

Note 1 to entry: In case of dynamic measurements, the term "frequency-temperature superposition" would be more accurate, but is less commonly used. The term "method of reduced variables" is also used to refer to this principle.

[SOURCE: ISO 18437-2:2005, 3.3, modified — "frequency axis" has been replaced by "logarithmic time axis" and Note 1 to entry has been added.]

3.6
thermorheologically simple material
material for which *time-temperature superposition* (3.5) is applicable

Note 1 to entry: A material which fails to superimpose, due to multiple transitions or crystallinity is, for example, thermorheologically complex.

Note 2 to entry: In thermorheologically complex systems, all relaxation times at a certain temperature may not be simply related to the relaxation times at a different temperature by a constant ratio. Thus, a multiphase system is thermorheologically complex if the individual *shift factors* (3.7) depend on time as well as temperature.

3.7
shift factor
$\lg a_T$
measure of the amount of shift along the logarithmic (base 10) axis of frequency for one set of constant-temperature data to superimpose upon another set of data

Note 1 to entry: The expression "shift factor" commonly refers to horizontal shift factor.

[SOURCE: ISO 18437-2:2005, 3.4, modified — Note 1 to entry has been added.]

3.8
vertical shift factor
$\lg b_T$
measure of the amount of shift along the logarithmic (base 10) axis of modulus to account the effect of a change from reference temperature to the temperature of interest

3.9
master curve
curve constructed by *time-temperature superposition* (3.5), which is identical to the behaviour of material that would be found (measured) at broad frequency range at the reference temperature if the experiment can be performed

4 Prediction of complete range of visco-elastic properties and description of data

4.1 Time-temperature superposition (TTS) principle

TTS is the most widely-used method for the accelerated prediction of complete visco-elastic behaviour of materials[13]. TTS is applied as follows: a series of dynamic mechanical experiments is carried out at different constant temperatures over a given short frame of frequencies, commonly called the experimental window. Thus, a set of isothermal segments of dynamic visco-elastic function is obtained. The isotherms are first shifted vertically, to account for temperature and density change and then horizontally along the logarithmic frequency scale towards a reference segment measured at reference temperature, T_R. The curve constructed by TTS is called a master curve. TTS asserts that the resulting master curve is identical to the behaviour of a material if it was measured with a broad frequency range at the reference temperature. The result of applying TTS to isotherms measured within experimentally reasonable frequency frames is a measure of material behaviour over a broad frequency range.

NOTE 1 Loss factor, as the ratio between loss and storage data, does not require vertical shifting[17].

There are several criteria for the applicability of TTS[13].

a) The shapes of the isotherms at different temperatures shall match over a substantial range of frequencies.

b) The same values of shift factor, a_T, shall superimpose all dynamic visco-elastic functions.

c) The temperature dependence of a_T shall be a smooth function of temperature with no gross fluctuations or irregularities.

NOTE 2 The temperature dependence of the shift function, a_T, is commonly modelled with time-temperature superposition models, such as Arrhenius[14] or Williams-Landel-Ferry (WLF)[13] relationships. More information on the WLF model is given in ISO 18437-4 and ISO 4664-1.

4.2 Data acquisition

4.2.1 New data

The acquisition of new data shall be sufficiently detailed with enough temperatures and frequencies so as to provide sufficient overlap of the frequency data points when shifted from one temperature to another. An example of good quality data are dynamic mechanical analyser (DMA) data taken every 5 °C using frequencies of: 0,1; 0,2; 0,3; 0,5; 1; 2; 3; 5; 10; 20; and 30 Hz and/or the dynamic data which has one decade of overlapping between neighbouring isotherms along the logarithmic frequency axis.

Theoretically, TTS is not limited to any frequency range of experimental window. However, the frequency range shall be selected in line with other existing standards and capabilities of a measuring instrument.

The temperature range shall be defined according to capabilities of an experimental setup, taking into account that the maximum temperature shall be limited to the temperature at which the sample still sustains its geometry, i.e. does not change geometry due to its own weight.

4.2.2 Existing data

If the existing data meet the criteria in 4.2.1, then they may be processed in the same way as new data. If the data are isochronal or do not have sufficient overlapping, then the corresponding experiments shall be carried out in accordance with the requirements given in this document.

If this is not possible, then an alternative method that is not part of this document can suffice[15] but shall not be construed to be part of this document.

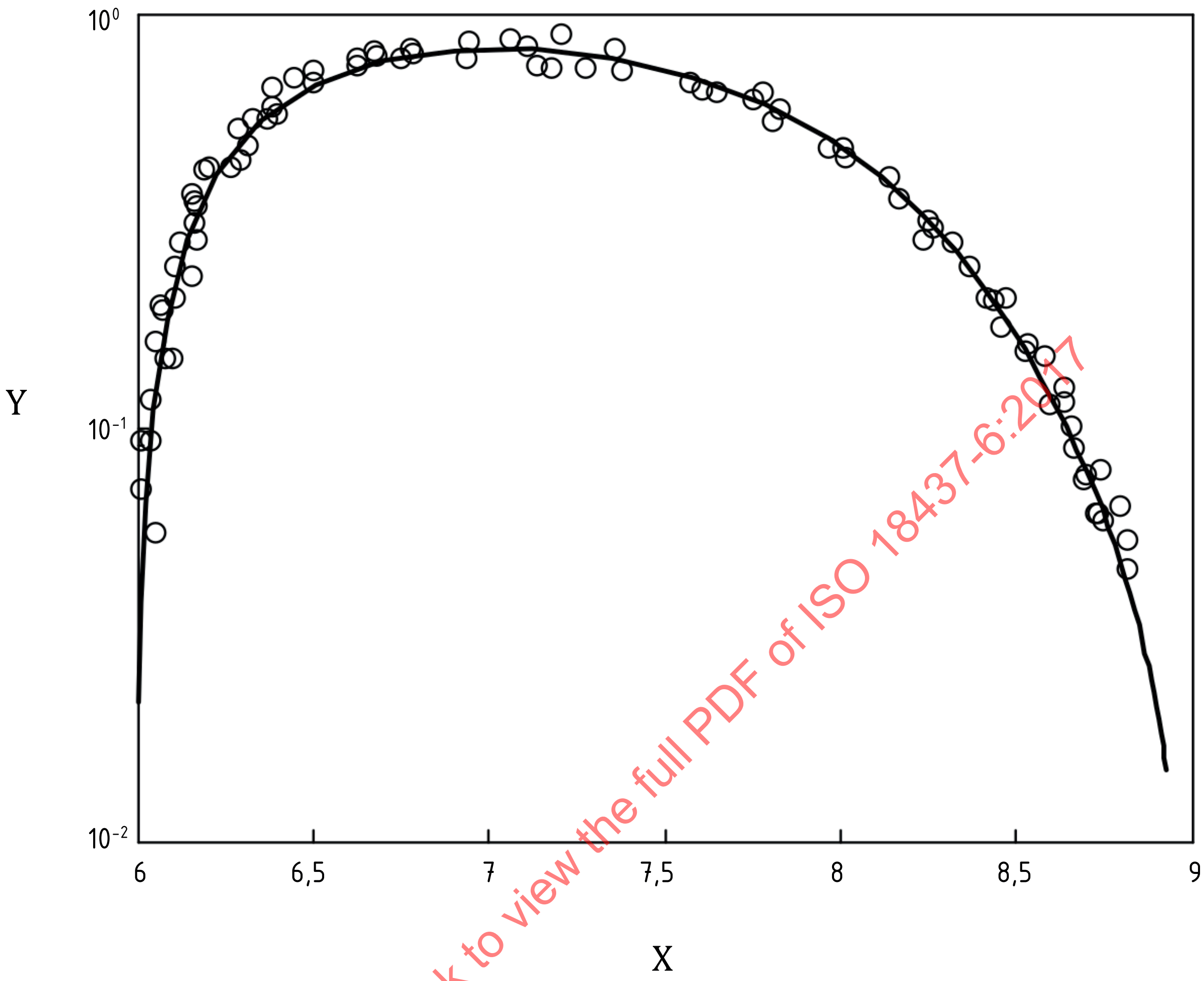
4.2.3 Data scatter and determination of thermorheological simplicity

If the material is thermorheologically simple, a_T is a smooth function of temperature with no gross fluctuations or irregularities and there is only one transition in the complete spectrum of frequencies and temperatures, then a plot of the loss factor versus storage modulus (called a wicket plot) will be a simple smooth curve, usually of an inverted "U" shape[15].

NOTE If there is more than one temperature transition in a polymer but all have the same shift function, a_T, then all the temperature and frequency data will still reduce to a single wicket plot curve but that curve will not be a simple single inverted "U".

The wicket plot shall be used as a quantitative indication of the scatter of experimental data. The width of the band of data, as well as the departure of individual points from the centre of the band, is indicative of scatter. Individual points that are sufficiently displaced from the smooth wicket plot band shall be removed or the data shall be repeated to determine its validity. Nothing is revealed about the accuracy of the temperature and frequency data or about any systematic error.

Figure 1 is an example of a wicket plot.



Key

X lg Young's modulus, in Pa

Y loss factor

Figure 1 — Example of a Wicket plot of computer-generated data for a high loss material with a maximum 10 % error in modulus and maximum 10 % error in loss factor

4.3 Shifting

4.3.1 Vertical shifting

Storage and loss data shall be firstly adjusted vertically and then shifted horizontally.

Frequently for solid visco-elastic materials the vertical shifting is small and may be ignored when forming master curves by TTS[14]. However, for some visco-elastic materials and/or certain testing conditions, e.g. broad temperature range, the vertical adjustment of dynamic visco-elastic functions can be significant. The lack of implementation of vertical shifting can lead to substantial errors in the prediction of properties over a wide frequency range. Therefore, vertical shifting shall proceed any horizontal shifting.

4.3.2 Horizontal shifting

The closed form shifting (CFS) algorithm[16][17] for calculation of horizontal shift factors shall be used whenever sufficient data are available to use this method. The method is based on the assumption that two neighbouring segments can be superimposed when the overlapping area between them is equal to zero.

The details of the method are beyond the scope of this document but are presented in Annex A and Annex B.

This methodology shall be used when implementing this document. As an example, a Microsoft® Excel[1)] macro with CFS methodology is included in Annex C.

4.3.3 Dynamic visco-elastic functions master curves

Criterion b) of the applicability of TTS (see 4.1) implies that the horizontal shift factors shall be defined from one function only. Since the storage modulus is usually measured more accurately and has less scatter than the loss modulus or loss factor, it shall be chosen for TTS. Horizontal shift factors determined from 4.3.2 shall be applied for shifting of other dynamic visco-elastic functions such as loss modulus and loss factor (see ISO 18437-2 and ISO 18437-3). It shall be taken into account that loss modulus, in the same way as storage modulus, requires vertical shifting.

A master curve of the storage modulus based on data measured at different temperatures is obtained by plotting $b_T M'$ versus $a_T \omega$ using base 10 logarithmic scale for both axes.

NOTE When the storage modulus is essentially flat, the loss modulus or loss factor can provide more accurate shifting. Corresponding formulae are available in Reference [17] but are not part of this document.

5 Verification

A check of the data consistency shall be done by plotting loss factor versus the logarithmic magnitude of the storage modulus without regard to temperature or frequency to verify that it is a single smooth band of data. For more details, see 4.3, ISO 18437-4 and ISO 10112.

The segments of dynamic visco-elastic functions to be shifted shall fulfil the TTS criteria in 4.1. If for any reason the criteria are violated, the TTS in its simple form as described in 4.1 shall be rejected; no master curve shall be drawn without subjecting the data to a more complicated analysis[13].

6 Main sources of uncertainty

6.1 General

Uncertainties of the shifting procedure (not the experimental technique) mostly follow from the anomalies in measured segments due to the weaknesses of the experiment itself, such as the improper sample preparation or sample treatment, bad clamping of the sample, improper implementation of the experiment or improper pre-processing of the data.

The main sources of uncertainties are described in 6.2 to 6.6.

6.2 Narrow width of overlapping between the segments (isotherms)

When the experiment yields segments with narrow overlapping, the shifting may result in the master curve and/or shift factors with a low precision. In this case, it is recommended to reestablish the experimental procedure that will yield segments with satisfactory overlapping (see 4.2.1).

1) Excel is the trademark of a product supplied by Microsoft®. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6.3 Presence of big experimental error (more than 10 %) in the segments

Since the master curve is usually composed of several curves, the cumulative error will be a sum of the errors of the individual segment shiftings. In the case of a high experimental error, the resulting master curve will contain a higher error than the original segments. Therefore, it is recommended to reestablish or change the selected experimental procedure that will yield segments with the acceptable, i.e. smaller, experimental error.

6.4 Low density of experimental datum points in the segment

A small number of datum points in the segment leads to poor approximation of the overlapping between the segments. It is recommended to reestablish or change the selected experimental procedure that will yield the number of datum points sufficient to describe all the peculiarities of the individual segment.

6.5 Inappropriately arranged input data — presence of "end effects" in the segments

When the experiment yields segments with certain anomalies at the beginning and/or at the end of the segment (segments with "end effects"), say, due to local overheating[18] or inertia effects[19], it is necessary to remove these anomalies before applying the shifting procedure. It is a matter of a critical judgement whether to exclude the complete segment or just a part representing the "end effects".

6.6 Selection of reference temperature

The most reliable master curve will be achieved when a central segment is selected as a reference segment. This is explained by the accumulation of error from segment to segment when shifting the data.

7 Results and processing

7.1 Data presentation

7.1.1 Data obtained in this document shall be presented in the form of several graphs and tables, as described in 7.1.2 to 7.1.6.

7.1.2 A graph of raw segments before shifting in double logarithmic (base 10) scale for moduli and in semi-logarithmic (lin-log) scale for loss factor.

7.1.3 A graph of a master curve at selected reference temperature in double logarithmic (base 10) scale for moduli and in semi-logarithmic (lin-log) scale for loss factor.

In order to promote uniformity and ease in interpreting the data at temperatures other than the reference temperature, it is recommended that the master curves of storage and loss moduli and loss factor are presented as a nomogram (see ISO 10112).

7.1.4 A table which contains

a) base 10 logarithm of horizontal shift factors for each segment, and

b) base 10 logarithm of vertical shift factors for each segment.

7.1.5 A graph of base 10 logarithm of horizontal shift factors as function of temperature at selected reference temperature.

7.1.6 A graph of base 10 logarithm of vertical shift factors as function of temperature at selected reference temperature.

7.2 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 18437-6;

b) all details necessary for complete identification of the material tested, type, source, manufacturer's code number or commercial name from any previous history, when these are known;

c) all details on methods, sample geometry and preparation used for input data measurements;

d) the estimated level of error (uncertainty) in the input data;

e) a table of raw data;

f) details on data treatment, if it was performed, e.g. elimination of bad input data;

g) the reference temperature for master curve generation;

h) the graphs and table described in 7.1;

i) the date of implementing the shifting procedure.

Annex A
(informative)

Closed form shifting (CFS) methodology

A.1 Vertical shifting

The vertical shift factor, b_T, is represented by the ratio shown by Formula (A.1):

$$b_T = \frac{\rho T}{\rho_R T_R} \tag{A.1}$$

where

T is the temperature of interest (K);

T_R is the reference temperature (K);

ρ is the density of a polymer at the temperature of interest (kg/m^3);

ρ_R is the density of a polymer at the reference temperature (kg/m^3).

In the case when the ratio of densities is not known, the vertical shift factor shall be defined as shown by Formula (A.2):

$$b_T = T / T_R \tag{A.2}$$

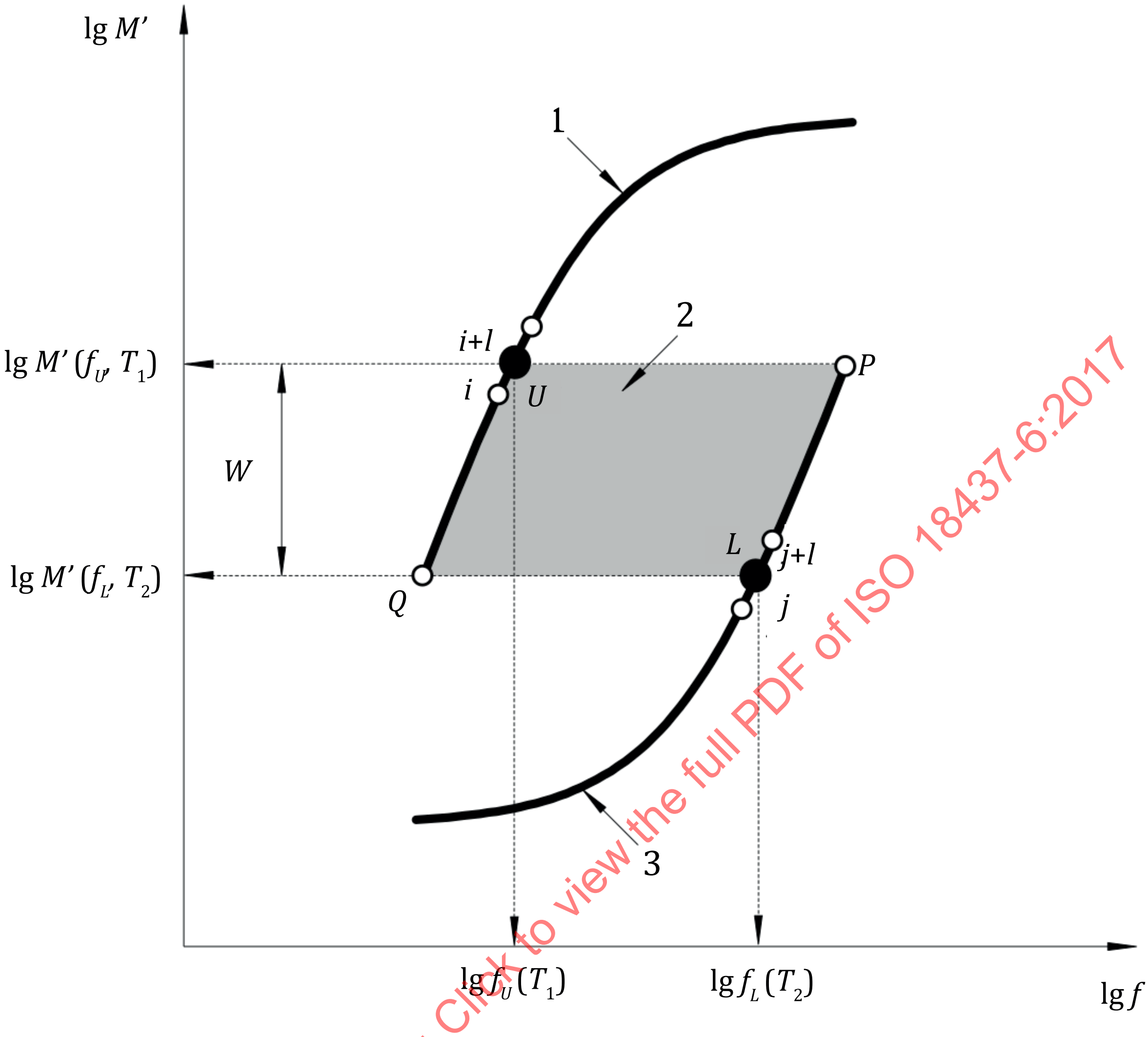
A.2 Horizontal shifting of two segments

The CFS methodology for calculation of horizontal shift factors is based on the assumption that two neighbouring segments can be superimposed when the overlapping area between them is equal to zero[16][17]. The overlapping area is an area between two adjacent segments, which is bounded from the left and right sides by overlapping parts of the segments and from top and bottom with the straight horizontal lines which connect the beginnings and the ends of overlapping portions of segments (shaded area, $A(T_1, T_2)$, in Figure A.1).

When the segments of storage modulus satisfy TTS criteria in 4.1, the width of the overlapping area, W, (Figure A.1) shall not be smaller than $\lg[(l+\varepsilon)/(l-\varepsilon)]$, where ε is the estimated experimental error[16][17].

Schematics of two monotonically increasing storage modulus segments, measured at two adjacent temperatures, T_1 and $T_2 > T_1$, are shown in Figure A.1 with N_1 and N_2 discrete datum points per segment, respectively.

According to TTS, to construct a master curve at the reference temperature, $T_R = T_1$, the segment measured at $T_2 > T_1$ should be shifted to the left along the logarithmic frequency axis, so as to obtain a smooth curve (see 4.1).



Key

1 storage modulus segment measured at reference temperature, T_1

2 overlapping area between segments, $A(T_1, T_2)$

3 storage modulus segment measured at temperature, $T_2 > T_1$

NOTE The notation, lg f (T_i), indicates the belonging of the frequency values to the segment, measured at temperature T_i.

Figure A.1 — Schematics of two storage modulus segments

The horizontal shift factor, $\lg \tilde{a}(T_2)$, corresponding to the segment measured at T_2 and further denoted as the "individual" horizontal shift factor, is calculated according to Formulae (A.3), (A.4) and (A.5):

$$\lg \tilde{a}(T_2) = \frac{\sum_{p=L}^{P-1} F_p(T_2) - \sum_{q=Q}^{U-1} F_q(T_1)}{\lg M'(f_Q, T_1) - \lg M'(f_P, T_2)} \tag{A.3}$$

where

$$F_q(T_1)=\frac{\lg f_q(T_1)+\lg f_{q+1}(T_1)}{2}\cdot[\lg M'(f_{q+1},T_1)-\lg M'(f_q,T_1)],q=Q,\ldots,U-1 \tag{A.4}$$

$$F_p(T_2)=\frac{\lg f_p(T_2)+\lg f_{p+1}(T_2)}{2}\cdot[\lg M'(f_{p+1},T_2)-\lg M'(f_p,T_2)],p=L,\ldots,P-1 \tag{A.5}$$

In the presence of experimental error, it might happen that the storage modulus curves will not have strictly monotonic behaviour, showing fluctuations. To eliminate the influence of the fluctuations in the computation of horizontal shift factor, the border points of overlapping area Q, P, U and L shall be defined as shown in steps a) to d).

a) Point Q is the minimum measured datum point of the segment at temperature T_1, as shown by Formula (A.6):

$$\lg M'(f_Q,T_1)=\min_q\{\lg M'(f_q,T_1),\ q=1,2,\ldots,N_1\} \tag{A.6}$$

b) Point P is the maximum measured datum point of the segment at temperature T_2, as shown by Formula (A.7):

$$\lg M'(f_P,T_2)=\max_p\{\lg M'(f_p,T_2),\ p=1,2,\ldots,N_2\} \tag{A.7}$$

c) Point U is an artificial point which represents the upper boundary of the overlapping section of the segment measured at temperature T_1. To find the frequency coordinate of point U, draw a horizontal line from point P towards the opposed segment measured at temperature T_1 and define the intersection. If the horizontal line crosses the opposed segment in several points, point closest in the sense of frequency to point Q shall be selected as the upper boundary point U. The frequency value of point U is as shown by Formula (A.8):

$$\lg f_U(T_1)=\lg f_i(T_1)+\frac{\lg M'(f_U,T_1)-\lg M'(f_i,T_1)}{\lg M'(f_{i+1},T_1)-\lg M'(f_i,T_1)}\cdot[\lg f_{i+1}(T_1)-\lg f_i(T_1)] \tag{A.8}$$

where i and i + 1 are the nearest to point U datum points (unfilled points in Figure A.1) of the segment measured at temperature T_1.

The storage modulus value of point U is shown by Formula (A.9):

$$\lg M'(f_U,T_1)=\lg M'(f_P,T_2) \tag{A.9}$$

d) Point L is an artificial point which describes the lower boundary of the overlapping portion of the segment measured at temperature T_2. To find the frequency coordinate of point L, draw a horizontal line from point Q towards the opposed segment measured at temperature T_2 and define the intersection. If the horizontal line crosses the opposed segment in several points, the point closest in a sense of frequency to point P shall be used as the lower boundary point L. The frequency value of point L is shown by Formula (A.10):

$$\lg f_L(T_2)=\lg f_j(T_2)+\frac{\lg M'(f_L,T_2)-\lg M'(f_j,T_2)}{\lg M'(f_{j+1},T_2)-\lg M'(f_j,T_2)}\cdot[\lg f_{j+1}(T_2)-\lg f_j(T_2)] \tag{A.10}$$

where j and j + 1 are the nearest to point L datum points (unfilled points in Figure A.1) of the segment measured at temperature T_2.

The storage modulus value of point L is shown by Formula (A.11):

$$\lg M'(f_L,T_2)=\lg M'(f_Q,T_1) \tag{A.11}$$

A.3 Master curve out of three or more segments

If experiments are performed at K different temperatures, i.e. $\{T_k, k = 1,2,...,K\}$, where $T_1 < T_2 < ... < T_K$ and $K \geq 3$, a smooth storage modulus master curve shall be constructed using the steps shown in a) to h).

a) Select a reference temperature, T_R, within the range of the experiment.

b) Shift vertically all the segments according to $\lg M'(f, T_k) - \lg b(T_k)$, $k = 1,2,...,K$, where $b(T_k)$ is given with Formula (A.1) or (A.2). In this way, vertically adjusted storage modulus values will be further denoted as "reduced" moduli.

c) For every pair of adjacent segments:

   1) define the frequency and reduced modulus values of points Q and P using Formulae (A.6) and (A.7), respectively;

   2) define the frequency and reduced modulus values of points U and L using Formulae (A.8), (A.9), (A.10) and (A.11), respectively;

   3) calculate individual horizontal shift factors, $\lg \tilde{a}(T)$, according to Formula (A.3) to (A.5). Always use the segment measured at lower temperature as a reference segment.

d) Set the "final" horizontal shift factor for reference segment to zero, i.e. $\lg a(T_R) = 0$. This means that the reference segment stays on its position.

e) Calculate the final horizontal shift factor for the segments measured at temperatures above the reference temperature, $T_m > T_R$, by summing up their individual horizontal shift factors with the final horizontal shift factor for the reference segment, i.e. as shown by Formula (A.12):

$$\lg a(T_m) = \lg a(T_R) + \sum_{r=R+1}^{m} \lg \tilde{a}(T_r) \tag{A.12}$$

f) Calculate the final horizontal shift factor for the segments measured at temperatures below the reference temperature, $T_n < T_R$, by subtracting individual horizontal shift factors from the final horizontal shift factor for the reference segment, i.e. as shown by Formula (A.13):

$$\lg a(T_n) = \lg a(T_R) - \sum_{r=n}^{R-1} \lg \tilde{a}(T_r) \tag{A.13}$$

g) Calculate "reduced" frequency values according to $\lg f(T_k) + \lg a(T_k)$, $k = 1,2,...,K$.

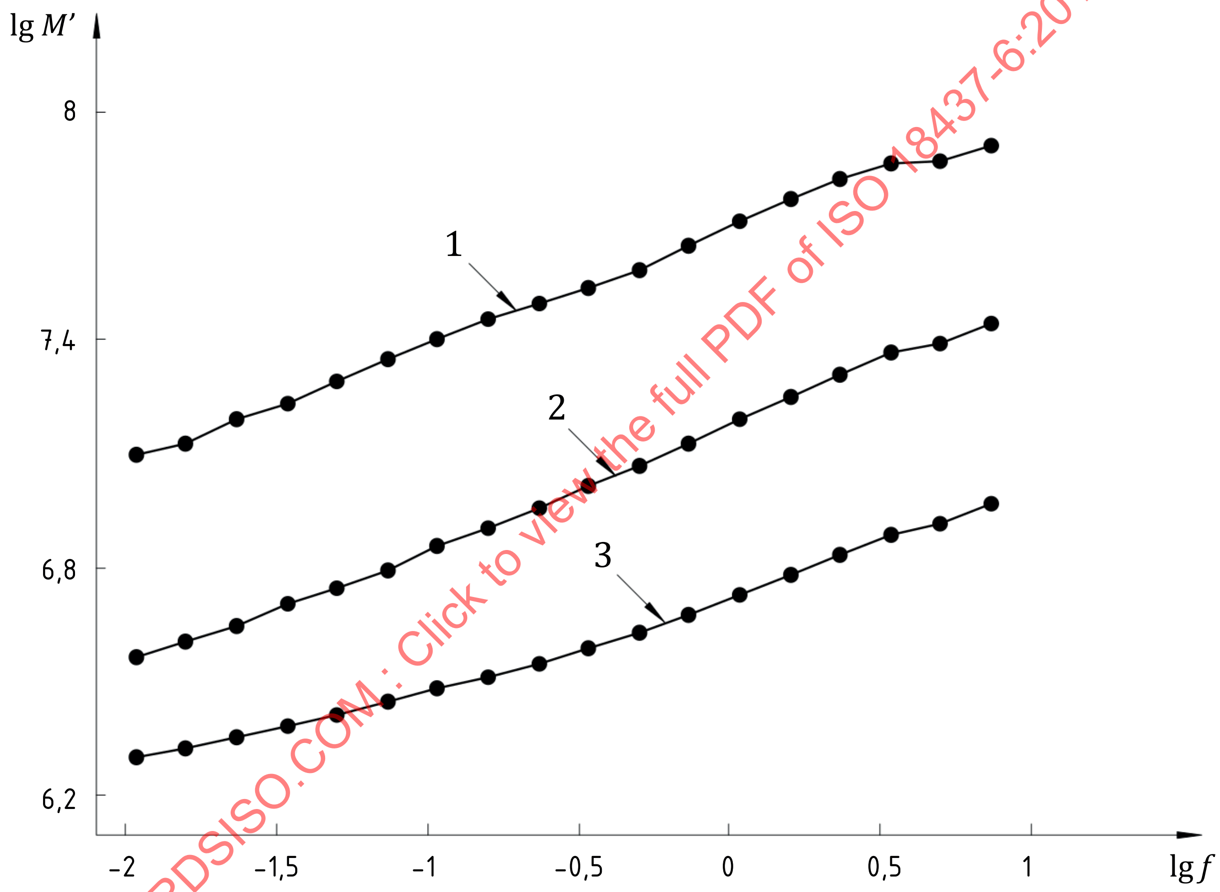
h) Plot the logarithmic (base 10) reduced modulus segments versus corresponding logarithmic (base 10) reduced frequency values, which will yield a smooth master curve.

An example of a master curve construction according to steps a) to h) is given in Annex B.

Annex B
(informative)

Example of storage modulus master curve construction

The example of application of shifting methodology for construction of the master curve presented in this annex examines three storage modulus segments measured at temperatures T_1 = 0 °C, T_2 = 10 °C and T_3 = 20 °C, which are given in Figure B.1 and Table B.1.



Key

1 storage modulus segment measured at temperature T_1 = 0 °C

2 storage modulus segment measured at temperature T_2 = 10 °C

3 storage modulus segment measured at temperature T_3 = 20 °C

Figure B.1 — Segments of storage modulus

Figure B.1 shows that the shape of the curves measured at different temperatures is the same, i.e. the criterion a) of TTS applicability (see 4.1) is fulfilled.

Table B.1 — Segments of storage modulus

#	lg f	T_1 = 0 °C	T_2 = 10 °C	T_3 = 20 °C
	lg f Hz	lg $M'(f,T_1)$ Pa	lg $M'(f,T_2)$ Pa	lg $M'(f,T_3)$ Pa
1	−1,964 8	7,094 6	6,565 7	6,300 5
2	−1,798 2	7,128	6,605 5	6,326 4
3	−1,631 5	7,187 7	6,649 3	6,351 8
4	−1,464 8	7,228 7	6,703 3	6,385
5	−1,298 2	7,291 5	6,748 6	6,413 7
6	−1,131 5	7,350 2	6,793 6	6,445 4
7	−0,964 9	7,400 7	6,858 1	6,482 6
8	−0,798 2	7,453 7	6,905 4	6,514 6
9	−0,631 5	7,492 6	6,959 1	6,549 7
10	−0,464 8	7,536	7,014 1	6,587 1
11	−0,298 2	7,584 4	7,070 2	6,631 7
12	−0,131 5	7,645 4	7,128 4	6,678 7
13	0,035 2	7,711 9	7,191 1	6,728 6
14	0,201 8	7,772 2	7,250 2	6,782 8
15	0,368 5	7,820 6	7,309	6,834 8
16	0,535 2	7,861 2	7,365 3	6,887 9
17	0,701 8	7,871 6	7,391 2	6,913 7
18	0,868 5	7,909	7,442 6	6,966 1

Table B.1 shows that all segments of storage modulus were measured within the same experimental window, i.e. $\lg f_n(T_1) = \lg f_n(T_2) = \lg f_n(T_3)$, for any n = 1, 2, ..., 18 and $N_1 = N_2 = N_3 = 18$.

To construct a smooth master curve, the steps a) to h) described in Annex A shall be followed.

a) Select a reference temperature, T_R, within the range of the experiments.

Let the segment measured at temperature T_2 = 10 °C be the reference segment, i.e. $T_R = T_2$.

b) Shift vertically all the segments according to $\lg M'(f, T_k) - \lg b(T_k)$, k = 1,2,3, where $b(T_k)$ is given with Formula (A.1) or (A.2).

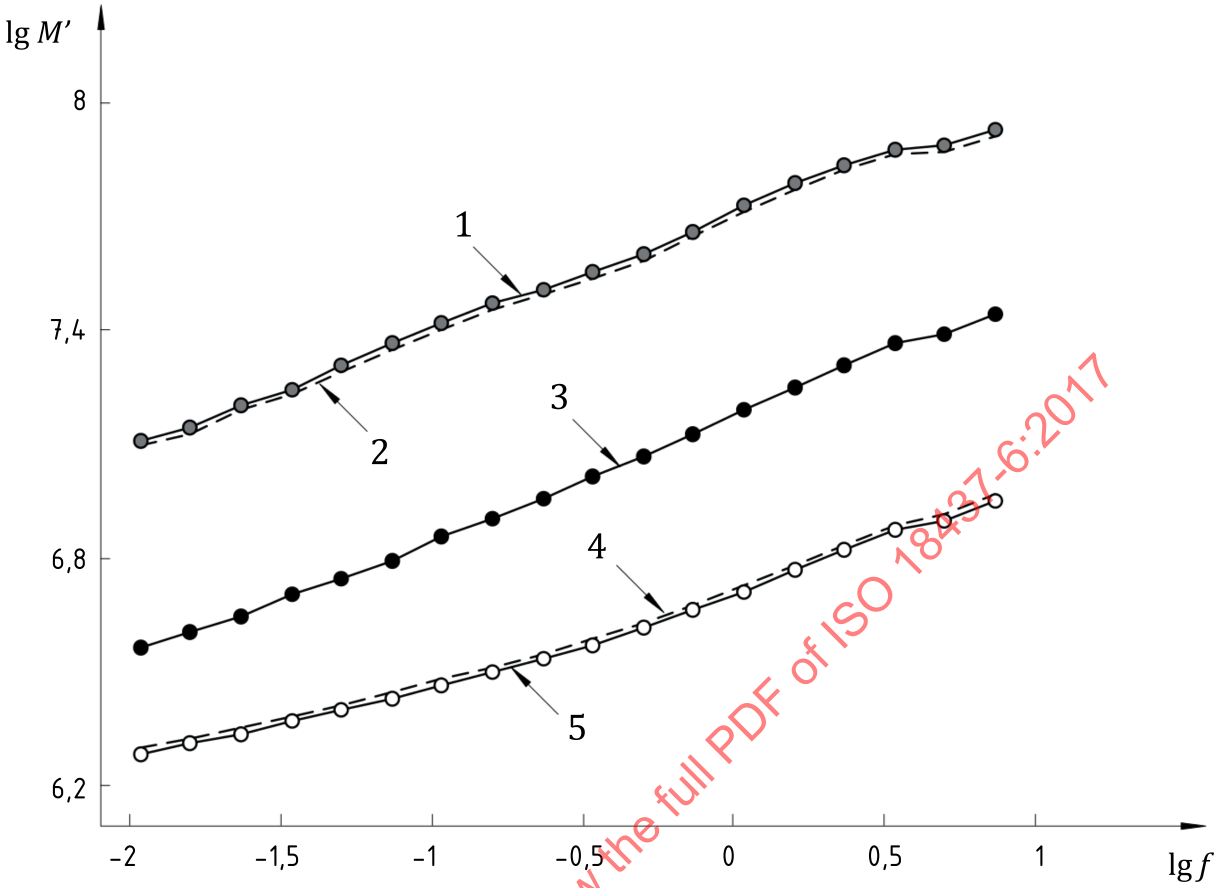
Since the density at different temperatures in the given example is not known, the vertical adjustment shall be performed according to Formula (A.2), i.e. $b(T) = T/T_R = T/T_2$, where the temperature values are given in Kelvin. Thus, the vertical shift factors are

1) $b(T_1) = (T_1 + 273{,}15)/(T_2 + 273{,}15) = 0{,}964\,7$ for the segment measured at temperatures T_1,

2) $b(T_2) = (T_2 + 273{,}15)/(T_2 + 273{,}15) = 1$ for the segment measured at temperature T_2 (which means the segment stays on its position), and

3) $b(T_3) = (T_3 + 273{,}15)/(T_2 + 273{,}15) = 1{,}035\,3$ for the segment measured at temperatures T_3.

Subtracting the vertical shift factor from the corresponding storage moduli (both in base 10 logarithm) gives the reduced storage moduli, which are shown in Figure B.2 and Table B.2.



Key

1 reduced storage modulus segment measured at temperature T_1 = 0 °C

2 original storage modulus segment measured at temperature T_1 = 0 °C

3 original storage modulus segment measured at (reference) temperature T_2 = 10 °C

4 original storage modulus segment measured at temperature T_3 = 20 °C

5 reduced storage modulus segment measured at temperature T_3 = 20 °C

Figure B.2 — Original and reduced storage modulus segments

Table B.2 — Reduced storage modulus segments

#	$\lg f$ Hz	T_1 = 0 °C $\lg M'(f,T_1)$ Pa	T_2 = 10 °C $\lg M'(f,T_2)$ Pa	T_3 = 20 °C $\lg M'(f,T_3)$ Pa
1	−1,964 8	7,110 2	6,565 7	6,285 4
2	−1,798 2	7,143 6	6,605 5	6,311 3
3	−1,631 5	7,203 3	6,649 3	6,336 7
4	−1,464 8	7,244 3	6,703 3	6,369 9
5	−1,298 2	7,307 1	6,748 6	6,398 6
6	−1,131 5	7,365 8	6,793 6	6,430 3
7	−0,964 9	7,416 3	6,858 1	6,467 5
8	−0,798 2	7,469 3	6,905 4	6,499 5
9	−0,631 5	7,508 2	6,959 1	6,534 6
10	−0,464 8	7,551 6	7,014 1	6,572
11	−0,298 2	7,6	7,070 2	6,616 6
12	−0,131 5	7,661	7,128 4	6,663 6
13	0,035 2	7,727 5	7,191 1	6,713 5
14	0,201 8	7,787 8	7,250 2	6,767 7
15	0,368 5	7,836 2	7,309	6,819 7
16	0,535 2	7,876 8	7,365 3	6,872 8
17	0,701 8	7,887 2	7,391 2	6,898 6
18	0,868 5	7,924 6	7,442 6	6,951

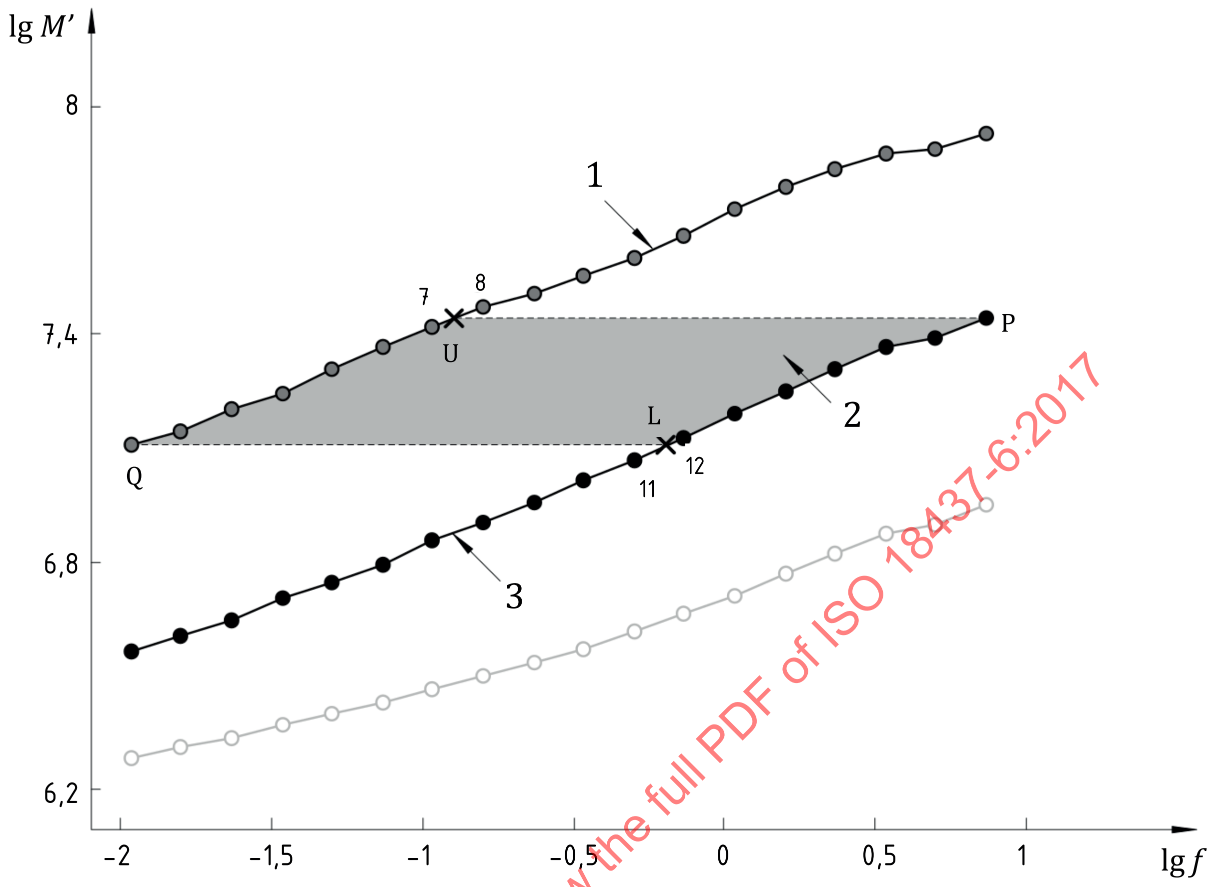
c) For every pair of adjacent segments:

1) define the frequency and reduced modulus values of points Q and P using Formulae (A.6) and (A.7), respectively;

2) define the frequency and reduced modulus values of points U and L using Formulae (A.8), (A.9), (A.10) and (A.11), respectively;

3) calculate an individual horizontal shift factors, $\lg \tilde{a}(T)$, according to Formula (A.3) to (A.5). Always use the segment measured at lower temperature as a reference segment.

Consider the first pair of reduced segments, which in this example corresponds to temperatures (T_1, T_2) = (0 °C, 10 °C) and which is highlighted in Figure B.3.



Key

1 reduced storage modulus segment measured at temperature T_1 = 0 °C

2 overlapping area, $\mathrm{A}(T_1, T_2)$

3 original storage modulus segment measured at temperature T_2 = 10 °C

Figure B.3 — Overlapping area of storage modulus segments measured at 0 °C and 10 °C

Points *Q* and *P*

The storage modulus value of point Q according to Formula (A.6) is

$$\lg M'(f_Q, T_1) = \min_q \{\lg M'(f_q, T_1),\ q = 1, 2, \ldots, 18\} = \lg M'(f_1, T_1) = 7{,}110\ 2\ \mathrm{Pa}.$$

The corresponding frequency value is

$$\lg f_Q(T_1) = \lg f_1(T_1) = -1{,}964\ 8\ \mathrm{Hz}.$$

The storage modulus value of point P according to Formula (A.7) is

$$\lg M'(f_P, T_2) = \max_p \{\lg M'(f_p, T_2),\ p = 1, 2, \ldots, 18\} = \lg M'(f_{18}, T_2) = 7{,}442\ 6\ \mathrm{Pa}.$$

The corresponding abscissa is

$$\lg f_P(T_2) = \lg f_{18}(T_2) = 0{,}868\ 5\ \mathrm{Hz}.$$

Points U and L

According to Figure B.3 and Formula (A.9), the storage modulus value of point U is

$$\lg M'(f_U, T_1) = \lg M'(f_P, T_2) = 7{,}442\,6 \text{ Pa}.$$

Whereas the frequency value calculated as per Formula (A.8) is

$$\lg f_U(T_1) = \lg f_7(T_1) + \frac{\lg M'(f_U, T_1) - \lg M'(f_7, T_1)}{\lg M'(f_8, T_1) - \lg M'(f_7, T_1)} \cdot [\lg f_8(T_1) - \lg f_7(T_1)] = -0{,}882\,2 \text{ Hz}.$$

The storage modulus value of point L given by Formula (A.11) is

$$\lg M'(f_L, T_2) = \lg M'(f_Q, T_1) = 7{,}110\,2 \text{ Pa}.$$

Whereas the frequency value calculated as per Formula (A.10) is

$$\lg f_L(T_2) = \lg f_{11}(T_2) + \frac{\lg M'(f_L, T_2) - \lg M'(f_{11}, T_2)}{\lg M'(f_{12}, T_2) - \lg M'(f_{11}, T_2)} \cdot [\lg f_{12}(T_2) - \lg f_{11}(T_2)] = -0{,}183\,6 \text{ Hz}.$$

Individual horizontal shift factor, $\lg \tilde{a}(T_2)$

The sums in the numerator of Formula (A.3) can be rewritten in the following way:

$$\sum_{q=Q}^{U-1} F_q(T_1) = \sum_{q=1}^{U-1} F_q(T_1)$$

where $F_{U-1}(T_1) = \dfrac{\lg f_7(T_1) + \lg f_U(T_1)}{2} \cdot \left[\lg M'(f_U, T_1) - \lg M'(f_7, T_1)\right]$

and

$$\sum_{p=L}^{P-1} F_p(T_2) = \sum_{p=L}^{17} F_p(T_2)$$

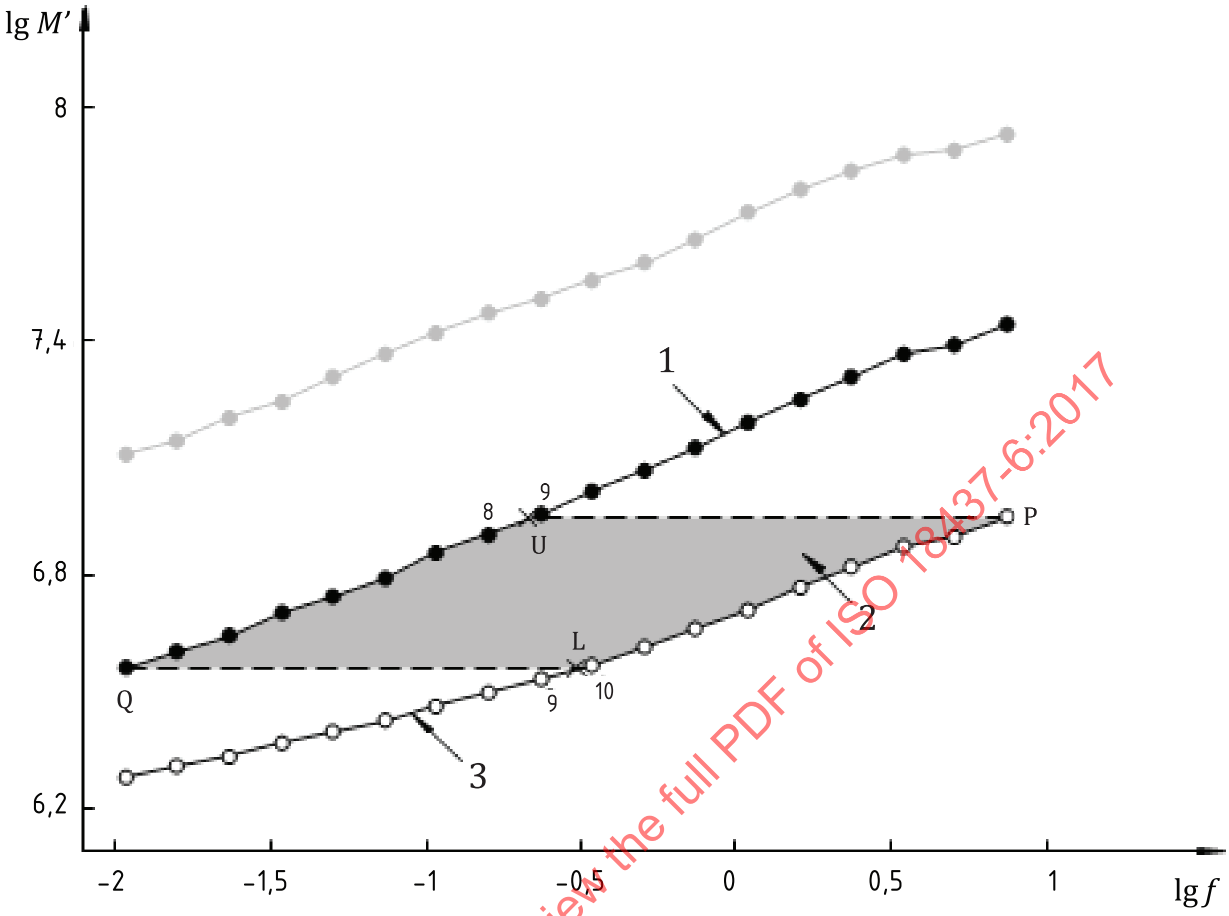
where $F_L(T_2) = \dfrac{\lg f_L(T_2) + \lg f_{12}(T_2)}{2} \cdot \left[\lg M'(f_{12}, T_2) - \lg M'(f_L, T_2)\right]$.

Thus, $\displaystyle\sum_{q=1}^{U-1} F_q(T_1) = -0{,}464$ and $\displaystyle\sum_{p=L}^{17} F_p(T_2) = 0{,}099\,7$.

Substituting obtained values of sums into the numerator of Formula (A.3), the individual horizontal shift factor between two storage modulus segments is equal to

$$\lg \tilde{a}(T_2) = \frac{\sum\limits_{p=L}^{P-1} F_p(T_2) - \sum\limits_{q=Q}^{U-1} F_q(T_1)}{\lg M'(f_Q, T_1) - \lg M'(f_P, T_2)} = \frac{0{,}099\,7 - (-0{,}464)}{7{,}110\,2 - 7{,}442\,6} = -1{,}695\,8.$$

Consider the second pair of reduced segments, which in this example, corresponds to temperatures (T_2, T_3) = (10 °C, 20 °C) and which is highlighted in Figure B.4.



Key

1 original storage modulus segment measured at temperature T_2 = 10 °C

2 overlapping area, $\mathrm{A}(T_2, T_3)$

3 reduced storage modulus segment measured at temperature T_3 = 20 °C

Figure B.4 — Overlapping area of storage modulus segments measured at 10 °C and 20 °C

For the pair of segments measured at temperatures T_2 and T_3, the steps are identical as for those measured at temperatures T_1 and T_2. All necessary values are given below.

Point Q: the storage modulus value according to Formula (A.6) is $\lg M'(f_Q, T_2) = \lg M'(f_1, T_2) = 6{,}565\,7\ \mathrm{Pa}$, the frequency value is $\lg f_Q(T_2) = \lg f_1(T_2) = 1964\ 8\ \mathrm{Hz}$.

Point P: the storage modulus value according to Formula (A.7) is $\lg M'(f_P, T_3) = \lg M'(f_{18}, T_3) = 6{,}951\ \mathrm{Pa}$, the frequency value is $\lg f_P(T_3) = \lg f_{18}(T_3) = 0{,}868\ 5\ \mathrm{Hz}$.

Point U: the storage modulus value is $\lg M'(f_U, T_2) = \lg M'(f_P, T_3)$, the frequency value is given by Formula (A.8) as linear interpolation between the 8th and 9th points of the segment, i.e.

$$\lg f_U(T_2) = \lg f_8(T_2) + \frac{\lg M'(f_U, T_2) - \lg M'(f_8, T_2)}{\lg M'(f_9, T_2) - \lg M'(f_8, T_2)} \cdot [\lg f_9(T_2) - \lg f_8(T_2)] = -0{,}656\ 6\ \mathrm{Hz}.$$

Point L: the storage modulus value is $\lg M'(f_L, T_3) = \lg M'(f_Q, T_2)$, the frequency value is given by Formula (A.10) as linear interpolation between the 9th and 10th points of the segment, i.e.

