



Research article

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Method for determining the thermal fluctuation constants of the generalized Zhurkov equation

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Abstract. Reliable forecasting of the service life of building materials and products allows you to lay down the costs of repair work in a timely manner, which in modern economic realities is undoubtedly an urgent task. This paper presents the results of a study on the development and comparison with existing methods for determining the thermal fluctuation constants of the generalized Zhurkov equation. A new method is proposed for determining the thermal fluctuation constants of the generalized Zhurkov equation. Practical application of the methodology will make it possible to reliably predict the service life of building materials. The main goal is to develop a method for determining the thermal fluctuation constants of the generalized Zhurkov equation, characterized by higher reliability by reducing the number of operations entailing errors, while increasing the number of experiments conducted under identical conditions (increasing the sample when determining durability under constant operating conditions). To achieve this goal, it is necessary to solve a number of tasks: 1) analyze the main provisions of the thermal fluctuation concept; 2) develop a method for determining the thermal fluctuation constants; 3) to conduct a comparative analysis of the obtained results of determining the thermal fluctuation constants. The object of the study is the constants of thermal fluctuation. The subject of the study is a new method for determining thermal fluctuation constants. The main methods of scientific knowledge used in the development of the methodology are hypothetical (the hypothesis of a linear dependence of the change slope of direct temperatures in the coordinates of the logarithm of durability - stress) and experiment (determination of durability of samples under transverse bending under specified operating conditions). A new method was developed for determining the thermal fluctuation constants of the generalized Zhurkov equation. It allows you to determine constants by plotting only one straight line temperature and one control point at a different temperature. Application of the proposed technique allows increasing the number of samples tested in identical conditions while reducing labor costs for experimental research. An increase in the sample leads to an increase in the accuracy and reliability of predicting the service life of building materials.

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1. Introduction

The problem of reliably predicting the durability of building materials, which is understood as the time before the onset of the limiting state, is one of the complex problems of construction science. The classical mechanical concepts of the strength of a material interpret the process of destruction as a critical event, the arrival of which is irreversible when the selected criterion of strength reaches its maximum value [1–5]. Otherwise, destruction is considered impossible, which contradicts reality [6–8]. In the middle of the last

century, many researchers have experimentally established, especially for polymer materials, the effect on the strength of the material not only by the time of stress action, but also by the ambient temperature [6, 9–13]. Thus the destruction occurred at values of stresses lower than the critical ones, however, such destruction took time.

S.N. Zhurkov was able to describe the observed temperature-time force equivalence of the destruction process by the formula, which was later named after him [6, 9]:

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma \cdot \sigma}{R \cdot T}\right). \quad (1)$$

And he was also able to reveal the physical meaning of the constants included in the resulting equation [6, 9]: τ_0 is constant, numerically close to the period of thermal vibrations of atoms; T is the absolute temperature; R is Boltzmann's constant; γ is structural-mechanical constant characterizing the geometric parameters of the material and the mechanical component of the fracture process; U_0 activation energy of the destruction process.

It was they who were proposed to consider the thermal motion of the kinetic units of a solid as a decisive factor in the process of destruction, while the mechanical component only ordered the process of oscillation of particles. This postulate formed the basis for the formation of first a kinetic and, subsequently, a thermofluctuation concept of fracture and deformation of solids.

S.B. Ratner and V.P. Yartsev modernized the Zhurkov equation (1) by introducing into it the limiting temperature of the existence of a rigid body without changing the interpretation of the role of thermal motion [14]. The equation is called the generalized Zhurkov equation:

$$\tau = \tau_m \cdot \exp\left[\frac{U_0 - \gamma \cdot \sigma}{R} \cdot (T^{-1} - T_m^{-1})\right], \quad (2)$$

where, τ is the durability of the material or the time until one of the limit states occurs, c; R is universal gas constant, kJ / mol • K; σ is stress, MPa; T is temperature, K; τ_m , U_0 , γ , T_m are physical constants of the material, having the following physical meaning for the classical case of convergence in a straight beam (Fig. 1.3, a): τ_m is the minimum time of destruction of a solid, characterized by the oscillation period of a particular kinetic unit (atom, group of atoms or segments), c; U_0 is the maximum activation energy of the destruction process, which is determined by the energy of bonds that prevents the loss of body integrity; moreover, in metals it is close to the sublimation energy, in polymers – to the activation energy of the thermal destruction process, i.e. the maximum activation energy of the destruction process is numerically close to the value of the activation energy for the decay of interatomic bonds in solids, kJ/mol; γ is structural-mechanical constant characterizing the efficiency of a mechanical field when a load is applied to the body kJ/(mol • MPa); T_m is the limiting temperature of the existence of a solid at which it decomposes in one thermal vibration, K.

Thus, it is possible to predict the durability of building materials within the framework of the thermofluctuation concept of fracture and deformation using formula (2). To predict the durability, it is necessary to know the four thermal fluctuation constants included in the generalized Zhurkov equation, which are determined by the graphic-analytical method from the experimentally obtained data on the dependence of durability (logarithm of durability) on the acting stresses and ambient temperature. To date, these constants have been established for a whole range of building materials [15–20]. However, the existing method for their determination is not distinguished by a high degree of reliability. This is due to the fact that according to the existing method for determining the constants, it is required to determine the durability (logarithm of durability) for each of three temperatures at five voltages. This is also due to the need to work in semi-logarithmic coordinates, when even minor deviations of the logarithm of durability in the zone of low durability (the range of experiments) leads to significant errors in further calculations of the durability of the material. The studies carried out on the example of polyvinyl chloride boards show that the values of the constants determined by different methods (graphical, graphic-analytical and mathematical) show significant discrepancies [21]. As well as the values of the constants obtained by different researchers on an identical array of initial data [22].

Thus, the main goal is to develop a method for determining the thermal fluctuation constants of the generalized Zhurkov equation, which is characterized by increased reliability due to a reduction in the number of operations entailing the appearance of errors, while increasing the number of experiments

conducted under identical conditions (increasing the sample when determining the durability under constant operating conditions).

To achieve this goal, it is necessary to solve a number of tasks:

- 1) to analyze the main provisions of the thermofluctuation concept;
- 2) to develop a method for determining thermofluctuation constants;
- 3) to carry out a comparative analysis of the results of determining the thermofluctuation constants obtained.

The object of study is thermoeluktuation constants.

The subject of the study is a new method for determining thermoeluctation constants.

2. Methods

To achieve this goal, it is necessary to check the hypothesis put forward (a hypothetical research method) that in the case of the invariability of the material structure in the entire temperature range, the tangent of the slope of direct temperatures in the coordinates $\lg \tau - \sigma$ obeys a linear relationship. The hypothesis put forward is verified theoretically, by the reverse method and experimentally.

For experimental verification of the hypothesis, polyvinyl chloride plates were chosen as the object of the study. This choice is due to the fact that it has a homogeneous structure and the presence of temperature-time force equivalence of the destruction process is clearly traced for it.

The dependence of durability (logarithm of durability) on stress and temperature was determined for polyvinyl chloride plates with transverse bending according to the following algorithm:

1. Determination of the critical load at which the durability is minimal.
2. Selection of the boundaries of temperature-force conditions based on the obtained critical load.
3. Determination of the durability of the material in the selected temperature and power conditions.

The studies were carried out on a six-position stand according to the standard method [20, 23]. The temperatures at which the measurements were carried out were 15, 30, 45 °C. For each temperature, five voltages are selected in the range from 0.75 to 0.95 of breaking. To obtain each point, at least 8 samples were tested under similar conditions. The results obtained were subjected to statistical processing according to the method according to Russian State Standard GOST R 8.736-2011 to eliminate gross errors and establish the boundaries of the confidence interval.

Thermofluctuation constants of the generalized Zhurkov equation were determined graphically, graphically, analytically, and mathematically according to the standard method [21].

3. Results and Discussion

The dependence of the logarithm of the durability on the effective voltage at constant temperature is linear and in general form can be written as follows:

$$\lg \tau(\sigma) = a \cdot \sigma + b, \quad (3)$$

where a is slope or tangent of the angle of inclination of a straight line, the physical meaning of which is the rate of the process; b is free term of the equation determining the logarithm of the life in the absence of stresses.

The absence of stresses in a solid is physically impossible, since the body's own weight creates stress in it. If in the idealized model we neglect the stresses from its own weight, then the value of the free term of equation (3) will determine the durability of the body in the absence of other types of stress.

When the temperature changes, the values of the coefficients of Eq. (3) will also change, and with increasing temperature a it increases, and b – decreases. With decreasing temperature, they respectively decrease and increase. The temperature of a body can vary in the range from absolute zero (0 K), which in practice, based on the provisions of thermodynamics, is unattainable, and the maximum temperature of the existence of a solid. Thus, the straight line of temperature corresponding to the temperature of absolute zero is located parallel to the ordinate of the graph plotted in the coordinates “logarithm of durability – stress” (Fig. 1). In this case, the coefficients of equation (3) tend to infinity, which is consistent with one of the main postulates of the thermofluctuation concept: the decisive factor in the destruction of a solid is the

thermal motion of kinetic units, and at a temperature of absolute zero, the process of motion stops [24]. The straight line of the maximum temperature of existence of a solid is parallel to the abscissa axis (stress axis) (Fig. 1). Consequently, the value of the logarithm of the durability is a constant value, which is equal to the oscillation period of the kinetic unit of a solid, and does not depend on the voltage. Thus, it seems logically justified to consider the change in durability between these limiting temperatures, since a negative temperature is impossible, and the study of behavior at temperatures above the temperature of the existence of a material has no physical meaning: the destruction of a solid requires a minimum time.

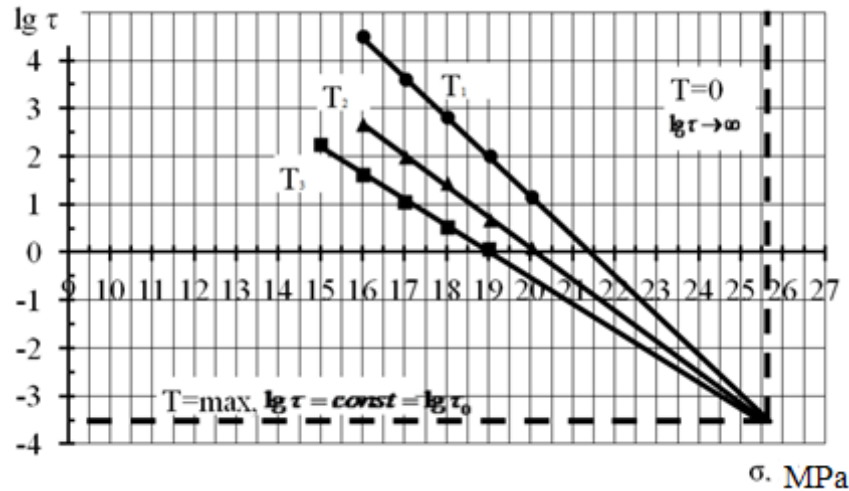


Figure 1. Example of a straight beam with boundary conditions.

If the structure of the material does not change over the entire temperature range under consideration, i.e. the thermal fluctuation constants of the generalized Zhurkov equation remain constant, according to the hypothesis put forward, the dependence of the change in the coefficient a of equation (1) on temperature or its inverse value is linear:

$$a = c \cdot T + d \quad (4)$$

or

$$a = c^* \cdot \frac{1}{T} + d^* \quad (5)$$

moreover, the dependence of the change in the coefficient b on temperature or its inverse value is also linear:

$$b = k \cdot T + \mu \quad (6)$$

or

$$b = k^* \cdot \frac{1}{T} + \mu^* \quad (7)$$

Straightness occurs only in the operating temperature range. So, when considering the dependence of the coefficient a on temperature at a temperature of absolute zero, the coefficient a tends to infinity (vertical asymptote), and at temperatures above the temperature of existence of a solid, the dependence has no physical meaning, since the body itself ceases to exist. In the case of considering the dependence of this coefficient on the reciprocal temperature, then at absolute zero the coefficient a linearly goes to infinity, and at the temperature of existence it crosses the abscissa axis and in the first positive half-quarter at temperatures above the temperature of existence of a solid body also has no physical meaning. The linear dependence of the coefficient b on temperature is also valid only up to the temperature of existence of a solid, at which it becomes an asymptote $\lg \tau_0$.

The hypothesis put forward is tested, as indicated earlier, in three ways: theoretical, proof from the opposite and practical. Let the dependences of the change in the coefficients of equation (3) be linear and described by equations (4) and (6), respectively, then substituting them into equation (3) we obtain:

$$\lg \tau = (c \cdot \sigma + d) \cdot T + k \cdot T + \mu \quad (7)$$

resolving which with respect to a variable T (temperature), taking into account that the voltage is in this case a constant value ($\sigma = const$), it turns out:

$$\lg \tau = (c \cdot \sigma + k) \cdot T + (d \cdot \sigma + \mu). \quad (8)$$

Thus, we have a linear relationship.

Similar actions with formulas (5) and (7) lead to a similar result:

$$\lg \tau = (c^* \cdot \sigma + k^*) \cdot \frac{1}{T} + (d^* \cdot \sigma + \mu^*). \quad (9)$$

Thus, the resulting equations (8) and (9) are forward stress equations constructed in the coordinate system of the logarithm of durability versus temperature (reciprocal temperature), which are obtained by rebuilding the graph in the coordinate system “ $\lg \tau - \sigma$ ” into the coordinate system “ $\lg \tau - T$ ” (“ $\lg \tau - \frac{1}{T}$ ”) practice. Consequently, the hypothesis put forward is confirmed.

In the case of proof from the opposite, let the dependences of the change in the coefficients of Eq. (3) are not linear, but obey, say, parabolic dependences. Then, solving equation (3) with respect to a variable at a constant voltage, the dependence of the logarithm of durability on temperature (reciprocal temperature) will not have a linear form, which contradicts the experimental data.

For polyvinyl chloride boards during transverse bending tests, the following direct temperatures of the dependence of the logarithm of durability on stress were obtained:

$$T = 15 \text{ }^\circ\text{C} - \lg \tau(\sigma) = -2.484 \cdot x + 15.766;$$

$$T = 30 \text{ }^\circ\text{C} - \lg \tau(\sigma) = -1.822 \cdot x + 11.366;$$

$$T = 45 \text{ }^\circ\text{C} - \lg \tau(\sigma) = -1.68413 \cdot x + 10.4504.$$

When constructing straight lines, the approximation method is used [25].

The change in the coefficient a obeys a linear relationship: $a(T) = 0.0267 \cdot T - 10.077$
 $\left(a\left(\frac{1}{T}\right) = -2466.6 \cdot \frac{1}{T} + 6.1573 \right)$, whose correlation coefficient is $R^2 = 0.8749$ ($R^2 = 0.8932$). The change in the coefficient b also obeys a linear relationship: $b(T) = -0.1772 \cdot T + 66.215$
 $\left(b\left(\frac{1}{T}\right) = 16390 \cdot \frac{1}{T} - 41.652 \right)$, which confirms the hypothesis put forward.

The constant T_m can be obtained from the boundary condition, at $a = 0$. Thus, the maximum temperature for the existence of PVC boards is 380 K (400 K). Substituting the limiting temperature in the dependence of the change in the coefficient b on temperature (return temperature), is determined $\lg \tau_0$. For polyvinyl chloride boards, it is:

$$b(T) = -0.1772 \cdot 380 + 66.215 = -1.121;$$

$$b\left(\frac{1}{T}\right) = 16390 \cdot \frac{1}{400} - 41.652 = -0.677.$$

The remaining two constants are proposed to be found by solving a system of equations in which the operating conditions (set from the operating conditions) and two constants are already known. For polyvinyl chloride boards, such a system of equations may look like this:

$$\begin{cases} 7.28 = 0.076 \cdot \exp \left[\frac{U_0 - \gamma \cdot 6.3}{8.314 \cdot 10^{-3}} \cdot \left((273 + 15)^{-1} - 380^{-1} \right) \right] \\ 107.152 = 0.076 \cdot \exp \left[\frac{U_0 - \gamma \cdot 5.3}{8.314 \cdot 10^{-3}} \cdot \left((273 + 45)^{-1} - 380^{-1} \right) \right]; \end{cases}$$

$$\begin{cases} 7.28 = 0.215 \cdot \exp \left[\frac{U_0 - \gamma \cdot 6.3}{8.314 \cdot 10^{-3}} \cdot \left((273 + 15)^{-1} - 400^{-1} \right) \right] \\ 107.152 = 0.215 \cdot \exp \left[\frac{U_0 - \gamma \cdot 5.3}{8.314 \cdot 10^{-3}} \cdot \left((273 + 45)^{-1} - 400^{-1} \right) \right] \end{cases}$$

Whence it follows that $U_0 = 409$ kJ/mol, $\gamma = 72.6$ kJ/mol MPa when working with a direct temperature and $U_0 = 329$ kJ/mol, $\gamma = 50$ kJ/mol MPa when considering the reverse temperature.

The obtained thermal fluctuation constants of the generalized Zhurkov equation by all methods are summarized in Table 1.

Table 1. A summary table of the found thermal fluctuation constants.

Method of determination	T_m , K	τ_m , c	U_0 , kJ/mol	γ , kJ/mol·MPa
Mathematical method [20–22]	400	0.177	313.4	47.15
Graphoanalytical method [20–22]	431	0.011	327.0	48.00
Graphical method [20–22]	390	0.180	370.0	58.00
According to the proposed method	380 (400)	0.076 (0.215)	409.0 (329.0)	72.6. (50.00)

Analysis of the values in Table 1 shows that the thermal fluctuation constants obtained by the proposed method correspond to the constants obtained by the previously used methods, including for other materials [7, 14, 15, 18, 19]. The smallest scatter associated with inevitable determination errors is observed when calculating the constants using the dependence of the inverse temperature on other parameters. The proposed technique allows reducing the errors in determining the constants due to the failure of working with graphs, and also simplifies mathematical calculations. At the same time, the high number of required experiments, each of which is associated with the appearance and accumulation of errors, remains the same. Even in studies that are not the largest in terms of volume, the number of necessary experiments exceeds a hundred. This fact does not greatly affect when working with a rapidly disintegrating material, but with an increase in the durability of the material, the time for conducting a single experiment greatly increases. All this results in many labor costs when receiving input data. Therefore, the next step is to reduce the number of experiments required to determine the thermal fluctuation constants of the generalized Zhurkov equation while maintaining high reliability of the results obtained.

The limiting temperature of existence can be obtained from the pole displacement equation:

$$\frac{1}{T_m} = \frac{c}{A \cdot \rho^2} + \alpha, \quad (10)$$

where c is heat capacity; α is thermal coefficient of linear expansion; ρ is density; A is characteristic of the forces of interatomic attraction.

Dependence (10) was theoretically substantiated by S.B. Ratner. S.N. Zhurkov also established a connection U_0 and γ with the fundamental characteristics of a solid:

$$U_0 = \left(\frac{c}{\alpha} \right) \cdot \varepsilon_0, \quad (11)$$

$$\gamma = \left(\frac{c}{\alpha \cdot E} \right) \cdot k, \quad (12)$$

where c is heat capacity; α is thermal coefficient of linear expansion; E is elastic modulus; ε_0 is the relative value of the limiting change in the interatomic distance leading to rupture; k is local link overload factor.

Determining the characteristics A , ε_0 and k in practice, cause difficulties and therefore the use of formulas (10), (11), (12) for determining the thermal fluctuation constants is limited. However, the limiting temperature of the existence of a solid can be obtained from the derivatogram.

The derivatogram is constructed in a research method called derivatography. Derivatography is based on a combination of differential thermal analysis with physical or physicochemical methods, such as thermogravimetry, dilatometry, mass spectrometry and emanation thermal analysis. Along with the transformations of the substance, which occur under the influence of the thermal effect, the change in the mass [26–28].

Thus, knowing the value of the limiting temperature of existence from the derivatogram, it seems possible and sufficient to determine the remaining thermal fluctuation constants to experimentally obtain a straight line of only one temperature in the “ $\lg \tau - \sigma$ ” coordinate system and the coordinates of one point at any other temperature. Knowing the values of the temperature (inverse temperature) and the value of the coefficient a of equations (4) and (5), as well as the limiting temperature of the existence of a solid, at which $a = 0$, it is necessary to solve the system of equations for c and d (c и d):

$$\begin{cases} a = c \cdot T + d \\ T_m = \frac{-d}{c} \end{cases}, \quad (13)$$

when, substituting the obtained coefficients into Eqs. (4) and (5), it seems possible to find the value of the coefficient a at the temperature (reciprocal temperature) at which the point is obtained experimentally. Then substituting the obtained coefficient into the formula (3), Further, substituting the obtained coefficient into formula (3), for which the operating conditions ($\lg \tau$ and σ) are known, the coefficient b is determined. Thus, the equation of the second line is obtained. The point of intersection of the lines gives the value of the coefficient $\lg \tau_0$. The remaining two thermal fluctuation constants are determined by solving the system of equations, which was shown earlier.

The required number of experiments to obtain one point, as well as the condition for the choice of the control temperature, at which only one point is determined, requires further study and justification.

4. Conclusion

1. A method has been developed for determining the constants of thermal oscillations of the generalized Zhurkov equation, based on the construction of only one direct temperature and one control point at another temperature.
2. It was found that the proposed technique allows to reduce the errors in determining constants due to the failure of working with graphs.
3. It is proved that the proposed method allows to reduce the number of experiments by almost 3 times.
4. It is established that the developed technique allows to increase the number of studies conducted at each point in comparison with the existing method at lower labor costs, which increases the accuracy of forecasting the durability of building materials.
5. It is established that the proposed method simplifies mathematical calculation.

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