JOINED STATISTICAL – THERMODYNAMIC EXPRESSION FOR ENTROPY AND HOOK'S LAW IN THE ANALYSIS OF STATES OF ELONGATED LIGAMENT BIOSTRUCTURE

by

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Analytic joined statistical – thermodynamic expression for entropy as a function of state for measuring the disorder of the corresponding micro state and the mechanical parameters which feature in the Hooke's law on elasticity as a measure of macro state was used in the situation of the isothermal elongation of viscoelastic ligament biostructure simultaneously with the external force of constant intensity to determine the change of entropy and the resultant reactive elastic force in the function of relative elongation. The sample used for the analysis and testing of the original joined theory shown with adequate equations is tested on linear biostructure approximating the data of Lig. collatelare fibulare which strengthens the lateral side of the knee joint. The obtained results for the tested linear biostructure according to which the minimal value of the difference in dS corresponds to the state of maximal entropy and the minimal value of elastic force indicates the acceptable level of elongation at which a reversible process is still possible, with low probability, are presented. This leads to the conclusion that, according to the results obtained here, the biostructure under examination can withstand the elongation which is approximately equal to twice the initial length L_0. *The relation between the friction force* F_{tr} *and the elasticity force* F_e *for the initial state is 1.0417, which indicates that the friction force is to a certain extent higher than the elastic force. With elongation, this ratio changes in favour of the friction force and becomes more prominent with advanced age.*

Key words: *entropy, Hook's law, ligament* bio-*structure, resistant elastic force, lig. collatelare fibulare, macro and micro changes*

Introduction

The application of Hook's law of elasticity in the biomechanical macroscopic examinations which are conducted under the influence of constant intensity external force *F* during the process of elongation of viscoelastic linear ligament biostructure (henceforth referred to as bio-structure) allows us to obtain *macroscopic* results which contribute to the better understanding of the anatomic, physiological and biomechanical characteristics [1]. However, Hook's law does not explain the influence of internal *micro* processes on the changes in biostructure which occur when it is elongated. These internal *micro* processes in

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the biostructure under the influence of external force F, at the temperature T, as a thermodynamic parameter, are indicated by a statistical value – entropy S as a measure of disorder of the corresponding micro state.

Since the process of elongation of ligament biostructure involves both the changes in the *macro* parameters which are featured in Hook's law and the changes in *micro* parameters from the expression of entropy, the aim of the present research is to integrate the above mentioned expressions into one. In this way, we would be able to simultaneously observe the changes in both *micro* and *macro* parameters when analysing ligament biostructure using one joined expression.

By the action of a constant external force, during the isothermal elongation of ligament bio-structure, an internal resistance force occurs within its molecules which opposes the elongation of the biostructure and, in reaction to it, tries to retain the original structure's shape and dimensions. This reaction force is *internal resistance elastic force* F^{*}_{eot} The intensity of this force is determined by using a joined analytical expression for the entropy S as a measure of *micro* state and the parameters in Hook's law as a measure of *macro* state [2, 3], which presents the subject of this paper.

When an external force F acts on a linear ligament bio-structure, the joined analytical expression enables us to simultaneously obtain the results indicating the changes of the entropy S, and the intensity of the force F_{eot}, as a function of relative elongation $\mathrm{d}L_0/L_0$. Knowing the value of F_{eot} it is possible to determine F_{e}, the elastic force of the bio-structure.

The original theoretical method for observing *micro* and *macro* states as functions of elongation presented in this paper was tested using the data which approximate *Lig. collatelare fibulare* which strengthens the lateral side of the knee joint.

The presented theoretical method which enables a simultaneous study of the changes in *micro* and *macro* states as a function of relative elongation can also be applied to other linear ligaments of viscoelastic bio-structure.

Theoretical basis

Entropy S, as a measure of disorder of the corresponding *micro* state of a structure, represents an internal characteristic of a bio-structure and depends on its length and temperature [4]. On the other hand, Hook's law of elasticity covers mechanical macroscopic parameters which describe *macro changes* in a bio-structure leading to elastic or plastic deformations.

We will assume that during the elongation process the temperature is constant (isothermal process) so that the change of the entropy dS is represented as a value which depends only on the initial length of bio-structure. If a bio-structure has an initial length L_0 and if, under the influence of external force F, it is elongated for dL_0, it obtains the length L_0 + dL_0. The differential of the change of the entropy dS between the two mentioned *micro* states L_0 and L_0 + dL_0 is:

$$\mathrm{d}S = S(L_0 + \mathrm{d}L_0) - S(L_0) \tag{1}$$

Developing the member $S(L_0 + \mathrm{d}L_0)$ in series according to the formula $f(a+b) = f(a) + b/1!\,f'(a) + b^2/2!\,f''(a) + \cdots$ we obtain that for the first two members of the series:

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[*] The term internal resistance elastic force F_{eot} *is* assumed to be the sum of two internal forces: the contribution of elastic force F_{e} and friction force F_{tr}, *i. e.* $F_{\mathrm{eot}} = F_{\mathrm{e}} + F_{\mathrm{tr}}$.

$$S(L_0 + \mathrm{d}L_0) = S(L_0) + \mathrm{d}L_0 \left(\frac{\partial S}{\partial L}\right)_{T,L=L_0} \tag{2}$$

where $\left(\frac{\partial S}{\partial L}\right)_{T,L=L_0}$ is the derivative of entropy with respect to length.

By replacing (2) into (1) it follows that:

$$\mathrm{d}S = \mathrm{d}L_0 \left(\frac{\partial S}{\partial L}\right)_{T,L=L_0} \tag{3}$$

In order to include the entropy S as a function of the *micro* state into the *macro* parameters of the Hook's law which is empirical in nature and does not indicate the influence of internal processes within the biostructure under elongation, we will start from the same law represented in the form [5, 6]:

$$\frac{\mathrm{d}F}{\phi} = E_y \frac{\mathrm{d}L_0}{L_0} \tag{4}$$

from which

$$\mathrm{d}L_0 = \frac{L_0}{E_y} \frac{\mathrm{d}F}{\phi} \tag{5}$$

where dF is the differential of the external force acting on the bio-structure, ϕ is the area of the cross-section of the linear biostructure which has the diameter much smaller than the length L_0 and E_y is Young's modulus of elasticity.

Inserting the expression (5) into the expression (3) we obtain that the change of entropy in the analysed process is as follows:

$$\mathrm{d}S = \frac{L_0}{E_y \phi} \left(\frac{\partial S}{\partial L}\right)_{T,L=L_0} \mathrm{d}F \tag{6}$$

Since, according to Helmholtz law, the effect of the force F when bio-structure is elongated for dL_0 is equal to the change of the entropy dS in the analysed process when $T = const.$ and $V = const.$, *i. e.*:

$$F\mathrm{d}L_0 = TdS \tag{7}$$

then substituting dS from (7) into (6) we obtain:

$$\frac{F}{T} \mathrm{d}L_0 = \frac{L_0}{E_y \phi} \left(\frac{\partial S}{\partial L}\right)_{T,L=L_0} \mathrm{d}F \tag{8}$$

Dividing eq. (8) by FL_0 we obtain the relationship between entropy and the parameters from Hook's law:

$$\frac{\mathrm{d}L_0}{L_0} = \frac{T}{E_y \phi} \left(\frac{\partial S}{\partial L}\right)_{T,L=L_0} \frac{\mathrm{d}F}{F} \tag{9}$$

In order to determine the derivation of entropy with respect to length in eq. (9) in the case when the length $L = L_0$, we need to first define the function of entropy of the one-dimensional bio-structure.

According to Boltzmann, the entropy S is defined as in [7]:

$$S = k_b \cdot \ln W \tag{10}$$

where $k_b = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant and W is the statistical probability of the initial state.

Based on the definition (10) and the adapted expression for statistical probability for the one-dimensional ligament bio-structure, we obtain the entropy expression S_0 which corresponds to the initial non-elongated state of the biostructure of the length L_0:

$$S_0 = \frac{k_b N}{2} \ln\left(\frac{\mathrm{e}}{\pi} \frac{k_b T}{2} \frac{L_0^2 M}{\hbar^2}\right) \tag{11}$$

where $\mathrm{e} = 2.718$ is the basis of a natural logarithm, $\hbar = 1.054 \cdot 10^{-34}$ [Js] is a constant, N is the number of molecules in the analytical biostructure of the volume $V_0 = \phi L_0$, M – the mass of bio-structure expressed in the unit atomic mass u, and T – the temperature.

Entropy S_0, for the initial sate of biostructure defined by the relation (11), corresponds to the internal, intermolecular force F_0 of the non-elongated structure of the length L_0. We will determine its analytical expression by the integration of eq. (7) within the limits for entropy from *0* to S_0 and the length from $L = 0$ to $L = L_0$ with the initial condition that $F = F_0$. After the integration and substitution of the expression (11) we obtain:

$$F_0 = \frac{T}{L_0} S_0 = \frac{T}{L_0} \frac{k_b N}{2} \ln\left(\frac{e}{\pi} \frac{k_b T}{2} \frac{L_0^2 M}{\hbar^2}\right) \tag{12}$$

The derivation of entropy with respect to length is according to (11):

$$\left(\frac{\partial S}{\partial L}\right)_{T, L = L_0} = \frac{\partial S}{\partial L_0} = \frac{k_b N}{L_0} \tag{13}$$

By substituting the expression (13) in (9) and noting that the volume $V_0 = \phi L_0$ is larger than the volume of the said *N* molecules and thus should be diminished for 10^{-2} m^3 (as an estimated value of the space volume, which belong to other, unspecified molecules present in V_0, *e. g.* molecules of liquids, *etc.*) we obtain for any elongated bio-structure of the length $L \geq L_0$ that:

$$\frac{\mathrm{d}F}{F} = \frac{E_y V_0 10^{-2}}{k_b N T} \frac{\mathrm{d}L}{L} \qquad \text{or} \qquad \frac{\mathrm{d}F}{F} = \gamma \frac{\mathrm{d}L}{L} \tag{14}$$

where

$$\gamma = \frac{E_y V_0 10^{-2}}{k_b N T} = \text{const.} \tag{15}$$

By integrating eq. (14) we obtain:

$$\ln F = \ln L^{\gamma} + \ln C \qquad \text{or} \qquad F = C L^{\gamma} \tag{16}$$

With the initial condition that $F = F_0$ and $L = L_0$ and relation (12) we obtain that the constant C in (16) is:

$$C = \frac{k_b N T}{2 L_0^{\gamma + 1}} \ln\left(\frac{e}{\pi} \frac{k_b T}{2} \frac{L_0^2 M}{\hbar^2}\right) \tag{17}$$

If the expression for the constant C according to (17) is substituted in (16) we obtain the required relation between the external force of the constant elongation F and the elongation of a one-dimensional bio-structure of the length $L \geq L_0$:

$$F = \frac{k_b N T}{2 L_0^{\gamma + 1}} \ln\left(\frac{e}{\pi} \frac{k_b T}{2} \frac{L_0^2 M}{\hbar^2}\right) L^{\gamma} \tag{18}$$

As long as bio-structure is under the influence of a constant external force F defined by the relation (18) it will be in a tensioned state. When the action of the force F stops in the region of the elastic deformation, the 1-D bio-structure will return to the initial steady-state of the length L_0. This means that, with the elastic deformation within bio-structure, as a reaction to the external force F, an internal resistance force F_{eot} appears having the same intensity but the opposing direction and being in equilibrium with the external force. In this way, according to the relation (18), the analytic expression for the resistant elastic force F_{eot} as a function of a change of entropy and length with the elongation of biostructure has the following form:

$$F_{\mathrm{eot}} = -\frac{k_b NT}{2L_0^{\gamma+1}} \ln\left(\frac{e}{\pi}\frac{k_b T}{2}\frac{L_0^2 M}{\hbar^2}\right) L^{\gamma} \tag{19}$$

In (19), the – symbol does not influence the intensity of F_{eot} but only indicates that the elastic internal resistance force F_{eot} has the direction which is opposite to the direction of the external force F.

Results and discussion

As an example of the application of the joined theory for determining the change in entropy and the resistant elastic force in the initial and elongated state, we analysed the linear ligament bio-structure with the data which approximate *Lig. collatelare fibulare* and which are shown in tab. 1.

In order to determine the number of molecules N within the analysed ligament bio-structure of mass m and volume V_0 ,which appears in expressions (11), (12) and (19), we will start from the assumption that the bio-structure in general consists of 95% collagen, 1% elastin and 4% connective tissue with the respective molar mass presented in tab. 1. Based on the given data and the share of collagen, elastin and connective tissue in the analysed bio-structure of mass m = 2 g, we get the total number of moles in the analysed biostructure $n = 0.82 \cdot 10^{-5}$ mol, which multiplied by Avogadro constant N_A , gives the number of molecules in biostructure $N = 10^{20}$ molecules.

Table 1. Values of parameters used for calculating entropy and elastic reactive force of reaction under the influence of external force of constant intensity on the structure of *Lig. collatelare fibulare*

Constant biostructure	Values	Approximate content and composition of biostructure	Value
Length, $\boldsymbol{L_0}$	$6 \cdot 10^{-2}$ [m]	<u>Collagen</u>: share of mass, m molar mass, M_k number of moles, n_k	95% 1.90 [g] $3 \cdot 10^5$ [g/mol] $6.33 \cdot 10^{-6}$ [mol]
Radius, $\boldsymbol{R}$	$5 \cdot 10^{-3}$ [m]		
Area, $\boldsymbol{\phi}$	$78.5 \cdot 10^{-6}$ [m^2]		
Volume, $\boldsymbol{V_0}$	$471 \cdot 10^{-8}$ [m^3]	<u>Elastin</u>: share of mass, m molar mass, M_{el} number of moles, n_{el}	1% 0.02 [g] $0.75 \cdot 10^5$ [g/mol] $2.66 \cdot 10^{-7}$ [mol]
Unit atomic mass, $\boldsymbol{1\,u}$	$1.6662 \cdot 10^{-27}$ [kg]		
Mass of analysed biostructure, $\boldsymbol{m}$	$2 \cdot 10^{-3}$ [kg]	<u>Connective tissue</u> share of mass, m molar mass, M_v number of moles, n_v	4% 0.08 [g] $0.5 \cdot 10^5$ [g/mol] $1.60 \cdot 10^{-6}$ [mol]
Mass of biostructure, m in $\boldsymbol{u\,M}$	$3.34 \cdot 10^{-27}$ [kg]		
Young's modulus, $\boldsymbol{E_y}$	10^6 [Pa]		
Temperature, $\boldsymbol{T}$	310 [K]	Total moles, n Total molecules, N	$0.82 \cdot 10^{-5}$ [mol] 10^{20} [molec.]
Avogadro constant, $\boldsymbol{N_A}$	$6.023 \cdot 10^{23}$ [molec./mol]		

On the basis of the data shown in tab. 1, and using relations (11), (12) and (19), it is possible to calculate the values of the resistant elastic force for the non-elongated (initial state) and elongated bio-structure. The dependence of the obtained values of F_{eot} as the function of elongation L is graphically represented in fig 1.

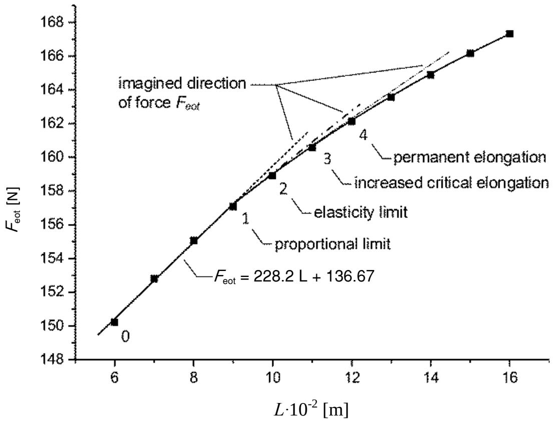

Figure 1. Dependency of resistant elastic force of linear ligament biostructure as a measure of macro state during the elongation of *Lig. collatelare fibulare*

On the basis of the obtained results, graphically presented in fig. 1, it can be concluded that *macro changes* in the analysed biostructure can be studied by looking at the changes in the resistant elastic force as a function of elongation of (6-10)$\cdot10^{-2}$ m. It can be noticed that the resistant elastic force in the initial non-elongated state (point 0) at the length $L_0 = 6\cdot10^{-2}$ m has the value $F_{\mathrm{eot}} = 150.28\,N$, that the proportional limit (point 1), until which linearity applies, corresponds to the resistant elastic force F_{eot} = 157.08 N and elongation $L = 9\cdot10^{-2}$ m, and that the elasticity limit (point 2) corresponds to the force $F_{\mathrm{eot}} = 158.91\,N$ and elongation $L = 10^{-1}$ m. The change of the resistant elastic force as a function of elongation from the non-elongated state (point 0) to the proportional limit (point 1) develops in a linear fashion, according to the equation $F_{\mathrm{eot}} = 228.2\,L + 136.67$, while, by the elasticity limit (point 2), the deviation from linearity is lower or higher than the simple proportionality law. After the elasticity limit, a non-linear increased critical elongation takes place (point 3) and then permanent deformation (point 4) and tearing.

Since entropy is, as a measure of *micro state*, defined according to the relation (11), for the initial non-elongated state L_0, at the elongation on L only differences (changes) of the entropy $\mathrm{d}S$ in relation to the initial state can be determined. These change $\mathrm{d}S = S_0 - S_L$, where $S_L = F_{L\,\mathrm{ot}}L/T$ for the individual *micro* states during elongation are represented graphically in fig. 2.

On the basis of the results presented graphically in fig. 2, it can be concluded that the analysed ligament bio-structure at isothermal elongation behaves, stated in simplified terms, as a viscoelastic polymer [8]. This means that the ligament bio-structure at isothermal elongation changes from the initial state L_0 into a less probable elongated state $L = L_0 + \mathrm{d}L_0$. Here the difference $\mathrm{d}S$ changes linearly with elongation (fig. 2), according to the equation $\mathrm{d}S = -0.49\,L + 0.0586$ so that at length $L = 11.95\cdot10^{-2}$ m the entropy change $\mathrm{d}S = S_0 - S_{11.95} = 0.12\cdot10^{-4}$ J/K. This difference of $\mathrm{d}S$ which tends to zero corresponds to the state of maximal entropy and thus, as a measure of *micro state,* it indicates that the length of the elongation $L = 11.95\cdot10^{-2}$ m is the final limit of the elastic elongation of the ligament biostructure for which there is still a limited possibility of reversible process [9]. Hence, the maximal value of entropy corresponds to the minimal negligible value of the elastic force $F_{e\,\mathrm{min}}$ which indicates an irreversible process. This leads to the conclusion that, according to the results obtained here, the tested linear bio-structure of *Lig. collatelare fibulare* can withstand elongation which is approximately equal to twice its initial length L_0 and at the same time maintain some minimal elastic properties which, with a certain low level of probability, may return it to the initial state.

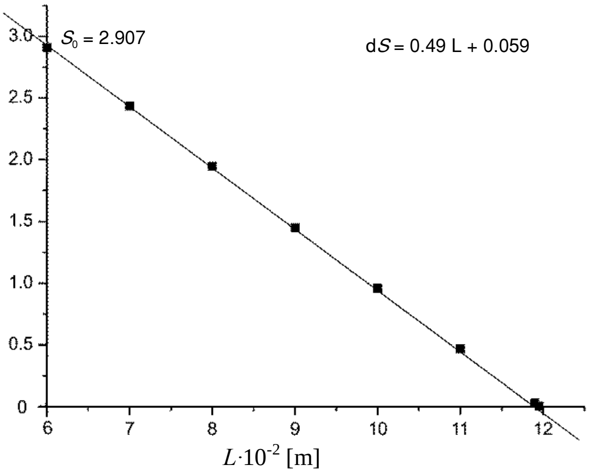

Figure 2. Entropy changes as a measure of micro states at the elongation of the linear biostructure of *Lig. collatelare fibulare*

The results of the present analysis of *Lig. collatelare fibulare* biostructure lead to the conclusion that it is extremely important to determine the share of the friction force F_{tr} and the bio-structure elasticity force F_e within the resultant internal resistant elastic force F_{eot}. This is significant because the age of the ligament biostructure changes the ratio between the friction force and the elasticity force in favour of the friction force. This means that, with older population, the behaviour of the ligament bio-structure under the influence of external force of constant intensity with elongations close to critical will be more likely to cause tear and avulsion of the bone [10]. For that reason, it is very important to determine the contribution of the friction force to the elasticity force of the bio-structure.

On the example of *Lig. Collatelare fibulare,* based on the relations established in [11], it is possible to approximate the ratio of the share of the friction force F_{tr} and the elasticity force F_e and show it for the initial non-elongated state as

$$\frac{F_{\text{tr}}}{F_e} = 1.0417 \tag{20}$$

The obtained relationship (20) indicates that the friction forces are somewhat larger than the elasticity forces. With elongation, this ratio changes, the friction increases, and the force of elasticity of the bio-structure decreases.

In order to determine the share of the elasticity force F_e as a function of ligament biostructure elongation, using the obtained results for the force $F_{\text{eot}} = F_e + F_{\text{tr}}$ as a function of elongation, fig. 1 and relation (20), we will start from the fact that for the critical elongation limit at $L = 11.95 \cdot 10^{-2}$ m, elasticity force $F_e \approx 0$, and for the initial non-elongated state $L_0 = 6 \cdot 10^{-2}$ m, $F_e = F_{\text{eot}}/2.0417 = 73.60\,N$. If we assume that the change of the elasticity force F_e as a function of biostructure elongation under the influence of an external force of constant intensity is basically linear, its intensity can be analytically determined by using the known values of the force F_e at points for $L = 11.95 \cdot 10^{-2}$ m and $L_0 = 6 \cdot 10^{-2}$ m as coordinates for finding the canonised form of equation of the line through two points. This linear dependency $F_e = f(L)$ is shown by the equation:

$$F_e = -1236.97\,L + 147.82 \tag{21}$$

and it allows us to calculate the intensity of F_e at any elongation $L \geq L_0$ within the range of $(6\text{-}11.95) \cdot 10^{-2}$ m.

The values of the dependency of the force F_e for the random positions within the above mentioned range with the elongated biostructure of *Lig. collatelare fibulare* determined using eq. (21) are shown in tab 2.

Table 2. Calculated values of the elasticity force F_e for random positions with the elongated *Lig. collatelare fibulare biostructure*

L [*10^{-2} m]	0.06	0.07	0.08	0.09	0.1	0.11	0.1195
F_e [N]	73.60	61.23	48.86	36.49	24.12	11.75	0.00

Conclusions

The results obtained in this research confirm the initial hypothesis that in the application of an external force of constant intensity on the linear viscoelastic ligament biostructure under elongation, using analytically obtained expressions (11), (12), and (19), it is possible to simultaneously observe the changes in entropy as a measure of *micro state* and the changes in the intensity of resistant elastic force as a measure of *macro state* as a function of relative elongation.

The relation of the friction force F_{tr} and the bio-structure elasticity force F_e for the linear bio-structure *Lig. collatelare fibulare* in the initial non-elongated state L_0 under the influence of a constant external force is 1.0417. This suggests that the friction force is to some extent higher than the bio-structure elasticity force and that at elongation this relation changes in favour of the friction force. This change becomes more prominent with the advanced age when, with older people, elongations closer to critical one are more prone to cause tear and avulsion.

The original theoretical method presented in this paper for simultaneous observation of changes in *micro* and *macro* states as a function of relative elongation of bio-structure can, because of its simplicity, be applied to other linear ligaments of viscoelastic bio-structure and can also be used as a starting point for future bio-structure research.

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