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Wood as a Thermodynamic System

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Summary

Wood is considered as a continuum whose behaviour must comply with basic laws of non-equilibrium thermodynamics. This provides a unifying point of view for explaining different processes in wood in terms of basic laws and constitutive assumptions. The equations governing the behaviour of wood under different circumstances (e.g. sorption, swelling, transport of moisture, build up of stresses) are derived from specific constitutive assumptions. More general constitutive assumptions compatible with requirements of non-equilibrium thermodynamics can lead to more realistic mathematical models.

Introduction

Wood is mostly treated for research purposes as a complicated biological and biochemical system whose behaviour is best explained in terms of the properties of the small structural units, such as cells comprising it. This approach, however fruitful from the point of view of pure science, can sometimes meet difficulties in explaining or rationally describing those phenomena which are characterized by complicated interactions between large numbers of structural units. Numerous papers dealing with such phenomena cover a wide range of problems including sorption and transport of moisture, swelling, and complicated interactions between external loads and temperature and moisture changes.

In such cases, it becomes advantageous to attack the problems using methods provided by phenomenological thermodynamics, which is not concerned with the internal structure of the material but deals instead with the properties of the system as a whole. Although much work has been done in separate areas, concerning for instance equilibrium sorption and swelling [Barkas 1950], or rheology and elastostatics of wood, no attempt to develop a synthetic approach from the point of view of modern non-linear thermodynamics is known to us.

Non-linear thermodynamics has been developed only recently and is connected with the names Truesdell, Coleman, Noll and others. Detailed and comprehensive information on this highly interesting subject can be obtained from monographs [Truesdell, Toupin 1960; Truesdell, Noll 1965] and original papers [e.g. Bowen 1967, 1968, 1969; Müller 1968; Coleman, Gurtin 1967; Coleman, Mizel 1966].

In following this approach, we start with the basic physical laws of conservation and with the constitutive equations which are regarded as equivalent to a definition of the material. It is shown how the conservation laws may be reduced in certain special cases to well known and widely used equations of wood physics, and the assumptions implicit in some of these equations are explicitly stated.

The aim of this paper is:

(1) To assist the process of cross-fertilization of some branches of science which are seldom, if ever, considered to be related, such as thermo-elasticity and the theory of wood drying, and chemical kinetics and stress relaxation.

(2) To show that many experimental results which were considered as untreatable by means of older theories [PERKITNY 1965] may now be explained in terms of a unified point of view.

(3) To encourage experimental studies which will provide the necessary material characteristics (independent of the size and shape of the sample) that are required for any improved description of wood behaviour and that will allow comparison with the equivalent characteristics of other materials.

Description of a Material as a Physical System

Variables

Work in an experimental science is based on the assumption that any experimental situation may be achieved at will by adjusting several parameters. The number and character of the parameters necessary to make the behaviour of a system deterministic differs from system to system. As a consequence of its biological origin, wood ranges amongst the most complicated of materials and may need a very large number or perhaps infinitely many parameters for its complete macroscopic description. Many of these parameters may not be easily accessible for measurement or, alternatively, their determination could be very tedious (e.g. the parameters describing all the changes in the biochemical and physical structure during loading, moistening, etc.). In such cases, it is useful to forego attempts to determine the complete set of parameters and instead to describe the system by means of the history of one or more of the variables already chosen. Theory indicates that the known past history of a sample provides us with substitute information for the equivalent of the unknown values of the "hidden" parameters. Effects of past history thus appear amongst the variables for a good reason and their presence does not need to be visualized by mechanical models with springs, dashpots and other elements. Apart from dependence on the history of deformation, which is already well recognized in wood research, we can also expect dependence on the histories of temperature [COLEMAN 1964] and perhaps of other variables, such as the concentrations of different components [ARIS 1967, 1968] to appear amongst the variables.

To describe any process in a given sample, it is sufficient to know how its measurable parameters vary in space (i.e. at different points of the sample) and time. The following quantities are usually considered as the most useful variables to describe a process:

Internal energy per unit mass of the system ε,
Entropy η,
Deformation function of each component χ_i,
($i = 1, \ldots, N$ where N is the number of components)
Density of each component ϱ_i,
Temperature ϑ,
Gradient of temperature g,
Gradient of density of each component h_i,
Flux of heat q,

Stress of each component T_i,
External forces acting on different components b_i,
External supply of energy per unit mass r,
Momentum supply of each component per unit mass $\hat{p}_i$,
Supplies of mass for each component by chemical reactions, $\varkappa_i$.

The list of variables just given need not be considered to be complete. This choice however makes it possible to take into account the most important phenomena. Other variables can be added if there arises a need to include some other, more peculiar features of behaviour.

Obviously, some of the variables such as temperature and density are scalars, some are vectors (g) and others are tensors (T). In agreement with an accepted convention, the scalars are mostly denoted by Greek minuscules, vectors by Latin minuscules and tensors by Latin majuscules.

The Field Equations

[TRUESDELL, TOUPIN 1960; TRUESDELL, NOLL 1965; BOWEN 1967, 1968, 1969; MÜLLER 1968].

Irrespective of the material in which they take place, all processes obey the basic laws of physics: the laws of conservation of energy, momentum, moment of momentum and total mass of the system. In addition to these conservation laws, the second law of thermodynamics (the Clausius Duhem inequality) must be valid.

The conservation laws are usually presented in the following form:

(a) Energy:

$$\varrho \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} + \operatorname{div} q - T : \operatorname{grad} v = \varrho r + \sum_{i}^{N} \varrho_i b_i u_i \tag{1}$$

where $\varrho = \sum_i \varrho_i$ is the total density $T : \operatorname{grad} v$ is equivalent to

$$\sum_{\alpha,\beta} T_{\alpha\beta} \frac{\partial v_\beta}{\partial x_\alpha}$$

v_i is the velocity of the i-th component

$v = \sum_i \frac{\varrho_i}{\varrho} \cdot v_i$ is the barycentric velocity

$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + v \frac{\partial}{\partial x}$ is the material derivative,

and $u_i = v_i - v$ is the diffusion velocity.

(b) Momentum:

$$\varrho_i a_i = \operatorname{div} T_i + \varrho_i b_i + \varrho \hat{p}_i,$$

$$\sum_i (\hat{p}_i + \varkappa_i u_i) = 0 \tag{2}$$

where $a_i = \frac{\partial^2}{\partial t^2} x_i$ is the acceleration of the i-th component.

The total stress T, i.e. the stress in the system as a whole, is obtained by summing the balance equations for the momenta of components.

Total stress is given by: $T = \sum_i T_i - \sum_i \varrho_i u_i u_i$

(c) Moment of Momentum:

$$T_{\varkappa\lambda} = T_{\lambda\varkappa} \text{ i.e. the tensor of total stress is symmetric } \varkappa, \lambda = 1, 2, 3 \qquad (3)$$

(d) Mass:

$$\frac{\partial \varrho_i}{\partial t} + \operatorname{div}(\varrho_i v_i) = \varrho \varkappa_i \qquad (4)$$

$$\sum_i \varkappa_i = 0$$

The Constitutive Equations

The equations of the preceding section cannot be solved without additional information as they contain too many variables. The additional information must also have the form of a set of relations connecting the same variables. These relations are called the constitutive equations. Whereas the field equations are basic laws of physics and therefore govern all processes in nature, the constitutive equations refer to the characteristic properties of a particular material, in our case wood. It is worth emphasizing that the constitutive equations do not depend on the size or shape of the sample or on external forces.

Given the complete set of constitutive equations for a particular material, it is possible to solve (in principle at least) the set of field equations for any given initial and boundary conditions (which include the geometry of the sample). The determination of the complete set of constitutive equations is therefore equivalent to defining the material.

We give the following as an example of a set of constitutive equations:

$$\begin{aligned} T_i &= T_i(D_j, \vartheta, g, \varrho_j, h_j, u_j - u_k) & q &= q(D_j, \vartheta, g, \varrho_j, h_j, u_j - u_k) \\ \varkappa_i &= \varkappa_i(D_j, \vartheta, g, \varrho_j, h_j, u_j - u_k) & \varepsilon &= \varepsilon(D_j, \vartheta, g, \varrho_j, h_j, u_j - u_k) \\ \hat{p}_i &= \hat{p}_i(D_j, \vartheta, g, \varrho_j, h_j, u_j - u_k) & \eta &= \eta(D_j, \vartheta, g, \varrho_j, h_j, u_j - u_k) \end{aligned} \qquad (5)$$

D_j is the tensor of deformation for each component.

In this example each dependent variable ($T_i, \varkappa_i \ldots$) is considered as a function of all independent variables. This is in agreement with the principle of equipresence which states that each independent variable should be considered to be present in all constitutive equations in the same way unless this is in contradiction to the second law of thermodynamics or to the principles of invariance [TRUESDELL, TOUPIN 1960, p. 704]. The principles of invariance are discussed in detail in the Encyclopedia of Physics [TRUESDELL, TOUPIN 1960, p. 700]. We shall mention two of them briefly. It is well known that the number of moduli of elasticity varies according to the symmetry of the material (from 21 for the most general anisotropic body to two for an isotropic one). This change is due to the requirement that certain transformations (rotations and reflections) must leave the response of the material invariant. The same requirement applies to all constitutive equations. Another type of limitation on the constitutive equations is imposed by the requirement of material indifference, i.e. that the response of the material should be independent of the position of the observer.

Use of the second law as a source of restrictions on constitutive equations was first made by COLEMAN and NOLL [1963] and this procedure was subsequently recognized to be a powerful tool for simplifying the constitutive equations [BOWEN 1967, 1968, 1969; MÜLLER 1968; COLEMAN 1964].

Special Cases

If all the constitutive Eqs. (5) for wood were known, the conservation laws together with the corresponding initial and boundary conditions could yield the mathematical description of any thermodynamic process in a given sample. However, the task of solving the complete system of partial differential equations is in general too difficult to perform. On the other hand, it is possible to find simpler situations where not all the field equations are needed and when the solution is consequently more accessible. As the most complicating factor in many problems in wood physics appears to be changing moisture content, we have chosen as illustrations of this approach two approximations concerning the manner of moisture content change. In the following section, we deal with cases in which the moisture content is constant or moisture content changes occur without significant gradients arising within the material. This would be the case for instance if the material were so thin that the process was essentially an interfacial one or if in thicker materials, rates of change of moisture content were very much slower [CHRISTENSEN 1965] than the possible rates of transfer by diffusion. The sub-section contains more detailed considerations obtained by making additional assumptions regarding the constancy of several other variables.

The overnext section, on the other hand, deals with cases where moisture gradients are present, and the resulting transport of moisture takes place in accordance with the equation of diffusion. Subsequent sections then deal with some special related cases.

Moisture Distribution Uniform

In the case of uniform distribution of moisture the velocities and deformations of all components are identical (or zero) and the equation for conservation of mass for each component is transformed [BOWEN 1968] into

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\varrho_i}{\varrho}\right) = \varkappa_i(\qquad\qquad) \tag{6}$$

The quantity $\varrho_i/\varrho = C_i$ is the concentration of component i and Eq. (6) is a differential equation well known from chemical kinetics.

It may be noted at this point that the set of differential Eqs. (6) together with the remaining constitutive equations can be given another meaning. It may be shown [COLEMAN, GURTIN 1967] that a set of equations of this form also describes the behaviour of a material with internal or "hidden" parameters. This in turn is equivalent to a description in terms of histories of accessible variables [COLEMAN 1964] as stated earlier.

In the present instance therefore, if there are some components present but neither they nor their concentrations are known, the system must be capable of interpretation as having internal variables. Whether the mathematics is in fact interpreted as a series of "chemical reactions" or as unknown internal "changes in structure" is a matter of choice which would only be significant if the nature of the internal changes in structure or alternatively the "chemical reactions" could be identified. This would be a formidable task in view of the complex molecular structure of the materials concerned. It is for this reason that the third equivalent stated above, namely the description of behaviour mathematically in terms of history of one or more variables, may be more suitable in the case of wood. The variable most eligible to be considered in this way is the total moisture content of the wood.

Swelling

In the previous section we were concerned with the case of only one of two independent processes taking place in wood: the sorption (represented by kinetic equations), while the other, swelling, was deliberately ignored. Here we intend to deal with the slightly more complicated case in which swelling can modify the sorption kinetics. The rate constants are now assumed to be dependent on deformation (degree of swelling). This dependence follows from the constitutive assumptions as presented earlier (see Eqs. 5). Hence, in this section the processes of swelling and sorption kinetics are coupled together and considered as one complex process.

In this case, in addition to the differential Eq. (6) we must take into account the equation for conservation of momentum:

$$\operatorname{div} T = 0 \tag{7}$$

which is obtained from Eq. (2a) by neglecting the acceleration and body forces.

The right-hand sides of Eq. (6) are given by constitutive equations in which the deformation is now included.

The quantitative description of uniform swelling could thus be obtained by simultaneous solutions of Eq. (6) and (7). The measure of swelling deformation depends on the choice of the standard state (deformed, undeformed) as is the case with deformations due to external forces.

(a) Free Uniform Swelling

Let us assume that there are only three components — dry wood with concentration (C_0), water (C_{w}), and wet wood (C_1), and let the sorption be given by a simple equation

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = k_1 C_0 C_{\mathrm{w}} - k_2 C_1 \tag{8}$$

C_0^0, C_1^0 are the initial concentrations of C_0 and C_1 respectively, and the rate constants k_1 and k_2 are in general dependent on deformation.

The linear constitutive equation for the total stress in an isotropic body is given by

$$T_{\varkappa\lambda} = \lambda \delta_{\varkappa\lambda}(D_{\nu\nu} - \gamma_1 c_0 - \gamma_2 c_{\mathrm{w}} - \gamma_3 c_1) + 2\,\mu D_{\varkappa\lambda} \tag{9}$$

where λ, γ_1, γ_2, γ_3, μ are constants and $D_{\nu\nu} = D_{11} + D_{22} + D_{33}$.

For swelling under hydrostatic pressure p, the solution of Eq. (7) will be

$$T_{\varkappa\lambda} = p\delta_{\varkappa\lambda} \tag{10}$$

where p is the external pressure.

The relationship between $D_{\varkappa\lambda}$ and C_0 can be obtained from Eq. (10):

$$3\,p = 3\,\lambda(D_{\nu\nu} - \gamma_1 c_0 - \gamma_2 c_{\mathrm{w}} - \gamma_3 c_1) + 2\,\mu D_{\nu\nu}$$

hence $D_{\nu\nu} = \dfrac{3\lambda}{3\,\lambda + 2\mu}\left(\gamma_1 c_0 + \gamma_2 c_{\mathrm{w}} + \gamma_3 c_1 + \dfrac{p}{2}\right)$ which can be written in terms of the compressibility modulus $k = \lambda + \dfrac{2}{3}\,\mu$:

$$D_{\nu\nu} = \frac{\lambda}{k}\left(\gamma_1 c_0 + \gamma_2 c_{\mathrm{w}} + \gamma_3 c_1 + \frac{p}{\lambda}\right). \tag{10a}$$

The trace of $D_{\varkappa\lambda}$ can be interpreted for small deformations as the relative change of volume: $D_{\nu\nu} = \dfrac{V - V_0}{V_0}$.

Corresponding formulae valid for an anisotropic body would be obtained by using appropriate constitutive equations instead of Eq. (9).

(b) Uniform Swelling Restricted in One Direction

Let us consider a swelling experiment with a wooden cube placed in between two parallel rigid plates.

The swelling will be calculated from the conditions that $u = 0$, $D_{11} = \dfrac{\partial u}{\partial x} = 0$ and from the constitutive Eq. (9). The solution of the equation of conservation of momentum in this case will be assumed in the form

$$T_{\varkappa\lambda} = 0 \quad \text{for} \quad \varkappa \neq 1,\ \lambda \neq 1$$

Hence:

$$2\,\mu D_{12} = 2\,\mu D_{13} = 2\,\mu D_{23} = 0$$

$$\lambda(D_{22} + D_{33} - \gamma_1 C_0 - \gamma_2 C_{\mathrm{w}} - \gamma_3 C_1) + 2\,\mu D_{22} = 0$$

$$\lambda(D_{22} + D_{33} - \gamma_1 C_0 - \gamma_2 C_{\mathrm{w}} - \gamma_3 C_1) + 2\,\mu D_{33} = 0$$

As $\mu \neq 0$ it must be that $D_{12} = D_{13} = D_{23} = 0$

and $D_{22} = D_{33} = \dfrac{\lambda}{2(\lambda + \mu)}\,(\gamma_1 C_0 + \gamma_2 C_{\mathrm{w}} + \gamma_3 C_1)$.

Finally the stress is given by

$$T_{11} = \frac{\lambda^2}{\lambda + \mu}\,(\gamma_1 C_0 + \gamma_2 C_{\mathrm{w}} + \gamma_3 C_1) - \lambda(\gamma_1 C_0 + \gamma_2 C_{\mathrm{w}} + \gamma_3 C_1).$$

The kinetics of swelling is again obtained by substitution of the solution of Eq. (8) for the concentrations.

Non-Uniform Distribution of Moisture-Diffusion Approximation

Another big group of problems deals with transport of moisture in wood in response to moisture gradients and with various associated phenomena. Transport of moisture below the fibre saturation point is usually described by means of the equation of diffusion [KOLLMANN, CÔTÉ 1968] whereas very little is known regarding the character of transport above the fibre saturation point—at least from the mathematical point of view.

However, objections have been raised to the uncritical use of the equation of diffusion. As mentioned earlier, CHRISTENSEN [1960, 1965] found for small specimens that sorption was controlled by a different mechanism, COMSTOCK [1963] showed that the diffusion coefficients obtained by different methods are different and MOSCHLER and MARTIN [1968], comparing predictions based on values of the diffusion coefficient taken from the literature with experimental data, found that the differences were excessive from the practical point of view.

These difficulties are not confined to the field of wood science as similar phenomena were also observed in other macromolecular systems [e.g. HAYES, PARK 1955; ALFREY et al. 1966; KWEI, ZUPKO 1969; MICHAELS et al. 1968; ROSEN 1960]. Some authors [ALFREY et al. 1966; HOPFENBERG, FRISCH 1969] suggested that different types of diffusion anomalies can be obtained according to the temperature and penetrant activity. We can, therefore, conclude that at least some difficulties are of a universal nature and should be explained without reference to the microstructure of the particular system.

Diffusion without swelling

The field Eqs. (1) — (4) with the corresponding constitutive equations must hold for any thermodynamic process including the transport of mass. The equation of diffusion should be therefore obtained from them as a special case, additional assumptions having been made. The derivation of the diffusion equation from the basic laws of physics was indeed made for a mixture of perfect fluids by TRUESDELL [1962]. To show which approximations are involved and, therefore, to specify the field of applicability of the diffusion equation we shall follow his idea, generalizing slightly to obtain a result for the mixtures of more complicated materials.

Diffusion and swelling

Let us observe first that the equation of balance of mass (Eq. 4) can be written as

$$\varrho \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\varrho_i}{\varrho}\right) + \operatorname{div}(\varrho_i u_i) = \varrho \varkappa_i$$

where the operator $\frac{\mathrm{d}}{\mathrm{d}t}$ is defined by

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + v \operatorname{grad}.$$

Fick's equation is obtained if $\varrho_i u_i = -D \operatorname{grad} \varrho_i$ where D is a positive constant called diffusivity [TRUESDELL, TOUPIN 1960, p. 706]. This was shown to be the case if $\hat{p}_i$ are linear functions of u_i and if the system can be considered as a mixture of ideal fluids with constitutive equations for stresses:

$$T_i = T_i(\varrho_i, \vartheta).$$

If, however, there is a solid component in the mixture, we can expect the stresses to depend on the deformation gradient F_s of the solid component. Hence

$$T_i = T_i(\varrho_i, \vartheta, F_s),$$

By inverting the linear constitutive equation for $\hat{p}_i$ we get

$$\varrho_i u_i = \varrho \sum_j G_{ij}(\hat{p}_j - \hat{p}_i)$$

where G_{ij} is a matrix of constant coefficients. If there are no body forces and the accelerations of components can be neglected, we get from the equation of conservation of momentum (Eq. 2):

$$\varrho \hat{p}_i = - \operatorname{div} T_i$$

and hence

$$\varrho_i u_i = \varrho \sum_j G_{ij} \operatorname{div}(T_i - T_j).$$

The divergence can be evaluated by using the constitutive equation for stress and we obtain

$$\varrho_i u_i = \varrho \sum_j G_{ij} \left[\sum_k \frac{\partial}{\partial \varrho_k} (T_i - T_j) \cdot \operatorname{grad} \varrho_k + \frac{\partial}{\partial \vartheta} (T_i - T_j) \cdot \operatorname{grad} \vartheta + \right. \\ \left. + \frac{\partial}{\partial F_s} (T_i - T_j) \operatorname{grad} F_s \right].$$

In the case of isothermal diffusion in a binary mixture of a fluid f and solid s, we can assume $\operatorname{grad} \varrho_s = 0$, $\operatorname{grd} \vartheta = 0$ and hence:

$$\varrho_f u_f = \varrho G_{fs} \left[\frac{\partial}{\partial \varrho_f} (T_f - T_s) \cdot \operatorname{grad} \varrho_f + \frac{\partial}{\partial F_s} (T_f - T_s) \cdot \operatorname{grad} F_s \right].$$

The first term corresponds to Fick's diffusion with the diffusivity

$$D = - \varrho G_{fs} \frac{\partial}{\partial \varrho_f} (T_f - T_s)$$

which depends on concentration and deformation gradient. The second term represents the deviation from Fick's diffusion due to non-uniform swelling. The dependence of diffusion on swelling is usually assumed negligible, though sometimes some influence of deformation of the wood on diffusion is acknowledged [HART 1964; KOLLMANN, CÔTÉ 1968, p. 224] whereas the connection between swelling and anomalous diffusion in polymers is generally accepted [ALFREY et al. 1966; HOPFENBERG, FRISCH 1969].

Diffusion and stress

The equations of conservation of momentum in a binary mixture can be written:

$$\varrho_1(a_1 - b_1) - \varrho_2(a_2 - b_2) + \operatorname{div}(T_1 - T_2) = \varrho(\hat{p}_1 - \hat{p}_2)$$

$$\varrho_1(a_1 - b_1) + \varrho_2(a_2 - b_2) + \operatorname{div}(T_1 + T_2) = 0$$

The combination of the former equation with the equation of continuity (12) was shown in the above sections to lead to the diffusion equation. The second equation is the equation of conservation of total momentum. The equation of diffusion is formally similar to the equation of heat conduction, and hence the combination of the equations of diffusion and of conservation of momentum is an analogy of equations describing the thermal stress phenomena.

Hence, if the use of the diffusion equation for the transport of one component (moisture in wood, say) is justified, the swelling stresses can be found by analogy with the theory of thermal stress. There is a vast number of practical problems already solved in this field which, we believe, could be used for handling corresponding problems of swelling stresses.

The exact stress analysis may sometimes be difficult but there are approximate procedures (for example, the theory of beams-columns based on the Bernoulli-Euler assumption that plane sections perpendicular to the axis remain so after loading) which can be very useful for engineering purposes. It may be noted that more complicated effects such as relaxation of swelling stresses, and residual drying stresses due to plasticity of wood can be taken into account. The reader can find detailed information in the monograph on thermal stresses [Boley, Weiner 1960].

Conclusions

1. The mathematical apparatus of nonlinear thermodynamics appears to be able to deal with many phenomena met in wood physics which until now were considered as quantitatively untreatable.

2. On the basis of nonlinear thermodynamics, it is clearly possible to distinguish between the properties of wood as a material and the design of the measuring apparatus, etc.

3. It is possible to give a set of constitutive equations which define the behaviour of wood. The exact form of these equations and the precision of the mathematical model as compared with various experiments is yet to be determined by further work.

4. By making simplifying assumptions, it is possible to derive approximate formulae which can be considered as generalizations of those already used.

5. The methods developed in other branches of science can sometimes be utilized in wood science on the basis of an analogy between variables, for example, as between moisture concentration and temperature.

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