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THERMODYNAMICS OF COMPLEX SYSTEMS: SPECIAL PROBLEMS OF COUPLED THERMAL AND MOISTURE FIELDS AND APPLICATION TO TAILORING OF COMPOSITES

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Abstract

In case of composites it is possible to increase the effectiveness of tailoring by involving new parameters, but utilizing special symmetries the enormous increase of needed numerical values can be avoided. Starting with the basic equations of thermo-hygro materials the special features and parameters are shown. Finally, some practical applications to the tailoring of fiber reinforced composites are displayed.

Keywords: thermo-hygro fields, Onsager relations, composites, tailoring

1. Introduction

The effectiveness of tailoring of composite materials requires the involvement of increasing number of parameters into the tailoring procedure. On the other hand, this growing number creates difficulties because to obtain the values of parameters is time consuming and very often a formidable task.

One possible solution of this problem is the following: broadening the possibility of tailoring by involving new parameters, but utilizing special symmetries the enormous increase of needed numerical values can be avoided. Such symmetries are well known in mechanics and thermodynamics, e.g., symmetry of stress tensor due to Newton's axioms; symmetry of strain tensor according to geometry; symmetry of stiffness matrix as a consequence of the two previous ones; symmetry of diffusivity and relaxation time matrices due to Onsager's reciprocal relations [1], [2]; symmetry of

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thermal and moisture expansion coefficient matrices based on the thermo-hygro-elastic (THE) constitutive equation (generalized Hooke's law) [6].

Our purpose was, starting with the general questions of coupled fields, to introduce the basic relations of thermo-hygro materials including the extension according to the second sound phenomenon [5]; to emphasize the features of thermo-hygro coupling and searching for the possible reasons of non-symmetry in coupled fields. Finally, the theoretical results were applied to tailoring of composite materials.

Fig. 1 shows a summary of the most often appearing fields and their couplings in mechanics of solids. Some of them are well known, others are in a fast developing process.

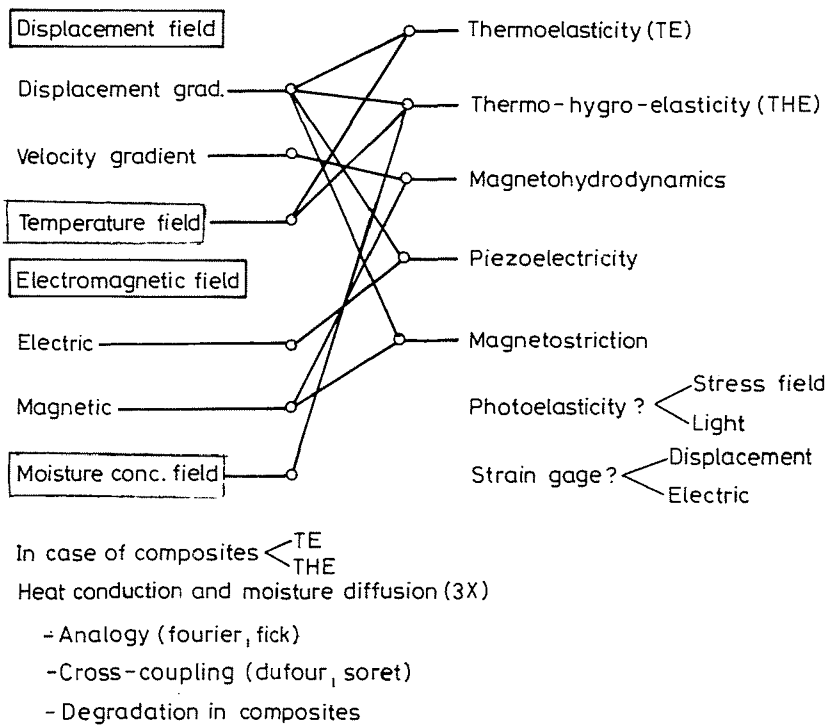

Fig. 1. Most frequent coupled fields of mechanics

E.g., thermo-hygro fields, always coupled with displacement fields, often occur in composite materials. In case of tailoring such materials the properties, especially the number thereof, have an important role.

Heat conduction and moisture diffusion have triple coupling:
- analogy between Fourier's and Fick's Laws,
- cross-coupling according to Dufour and Soret effects,
- similar effect on degradation in composites.

Let us see the basic equations of thermo-hygro materials [5].

2. Basic Problems of Thermo-Hygro Materials

The independent variable of thermo-hygro materials must satisfy the conservation laws

$$\rho_1 \dot{C} = -\nabla \cdot \underline{J}^c + \sigma^c \tag{2.1}$$

and constitutive laws

$$\underline{J}^c = -\alpha^c \nabla C. \tag{2.2}$$

Here $\underline{J}^c$ and σ^c stand for the flux and source terms, respectively, corresponding to $C; \rho_1$ and α^c are the coefficients; a dot denotes the material time derivative and ∇ the space derivative. We apply these equations for moisture and temperature. Further considerations of this section are based on [5]. *(i) Moisture and Fick's Law*

Replacing the thermal variables and coefficients of *Eqs.* (2.1) and (2.2) with their equivalents in terms of moisture: $C = m$ the moisture concentration at a certain point of a solid; $\underline{J} = \underline{f}$ the moisture flux, $\rho_1 = 1, \sigma = 0$ and $\alpha = D_m$ the moisture diffusion coefficient. With these notations, *Eqs.* (2.1), (2.2) read

$$\nabla \cdot \underline{f} + \dot{m} = 0, \tag{2.3}$$

$$\underline{f} = -D_m \nabla m. \tag{2.4}$$

Substituting (2.4) into (2.3) we obtain

$$\dot{m} = D_m \nabla^2 m \tag{2.5}$$

Eqs. (2.4) and (2.5) are called Fick's First and Second Laws. *(ii) Temperature and Fourier's Law* Let $C = T$ that is the temperature at a certain point of a solid. The other notations are then: $\underline{J} = \underline{q}$ is the heat flux, $\rho_1 = \rho c_p$, where c_p is the specific heat with respect to the volume and ρ is the density; as above, σ is neglected and $\alpha = k$ is the coefficient of heat conduction. Equation (2.1) emphasises then the conservation of energy

$$\nabla \cdot \underline{q} + \rho c_p \dot{T} = 0 \tag{2.6}$$

while *Eq.* (2.2) is the celebrated Fourier's Law

$$\underline{q} = -k \nabla T \tag{2.7}$$

Substituting (2.7) into (2.6), the heat conduction equation yields

$$\dot{T} = D_T \nabla^2 T. \tag{2.8}$$

Here $D_T = k/\rho c_p$.

The similarity between the final results (2.5) and (2.8) is obvious, as well as between the (first) Fick's Law and the Fourier Law. It means actually that theoretical, numerical, and experimental problems of moisture and temperature diffusion can be treated in a similar way.

An interesting question arises about the simultaneous transport of moisture and temperature: are the effects caused by these phenomena coupled or not? The answer is given in the following section. *(iii) Coupling between heat and moisture transport* There is experimental evidence that the temperature field affects the moisture transport, and vice versa, moisture concentration affects the temperature field. First, the heat flux, caused by moisture concentration gradient

$$\underline{q} = -\alpha_T^m \nabla m \tag{2.9}$$

is associated with the Dufour effect, while the corresponding flux is called the Dufour flux. Secondly, the moisture diffusion due to temperature gradient

$$\underline{f} = -\alpha_m^T \nabla T \tag{2.10}$$

is associated with the Soret effect with the corresponding flux being the Soret flux. Here α_T^m, α_m^T are the coupling diffusion coefficients: diffusion-thermo and thermal-diffusion coefficients, respectively. Suppose we add the Dufour and Soret fluxes to our basic equations in the previous section. The coupled fluxes can then be written in the following form

$$\underline{J}_i = -\alpha_{ij} \nabla C_j \tag{2.11}$$

and the coupled final equations (provided α_{ij}'s are constant)

$$\dot{C}_i = D_{ij} \nabla^2 C_j + \sigma_i, \tag{2.12}$$

where the summation convention over the repeated indices is used, $i, j = 1, 2$. The notation is obvious:

$$\begin{array}{llllllll}
\underline{J} & = f, & \underline{J}_2 & = \underline{q}; & & & & \\
C_1 & = m, & C_2 & = T; & & & & \\
\alpha_{11} & = \alpha_m, & \alpha_{12} & = \alpha_m^T, & \alpha_{21} & = \alpha_T^m, & \alpha_{22} & = k; \\
D_{11} & = \alpha_m, & D_{12} & = \alpha_m^T, & D_{21} & = \frac{\alpha_T^m}{\rho c_P}, & D_{22} & = \frac{k}{\rho c_P}.
\end{array}$$

It should be noted that *Eq.* (2.12) is the system of coupled hygro-thermal equations following the principle of equipresence. In addition, the Onsager's relation for α_{ij} can be added

$$\alpha_{12} = \alpha_{21}.$$

3. Special Features of Thermo-Hygro Coupling

The paradox of the heat conduction equation (2.8) is well known. Because of its parabolic character (2.8) predicts infinite speed of heat propagation which contradicts physical principles. Maxwell has pointed out the solution to this paradox but contemporary understanding is based on ideas of Vernotte and Cattaneo who introduced relaxation time for the heat flux into the basic equation (2.7).

The basic (more or less formal) solution to this paradox is the following. Instead of *Eq.* (2.7) we use

$$\underline{q} + \tau_T \dot{\underline{q}} = -k\nabla T, \tag{3.1}$$

where τ_T is the relaxation time. Introducing (3.1) into (2.6), we obtain

$$\dot{T} + \tau_T \ddot{T} = D_T \nabla^2 T \tag{3.2}$$

which is a hyperbolic equation, describing wave motion with a finite speed

$$c_T = (D_T/\tau_T)^{1/2}. \tag{3.3}$$

The striking analogy between the basic models of moisture and heat transport (*Eqs.* (2.5), (2.8)) leads logically to formal generalizations.

First, we are tempted to generalize the constitutive law (2.2)

$$\underline{J}^c + \tau^c \dot{\underline{J}}^c = -\alpha^c \nabla C, \tag{3.4}$$

where τ^c is a certain relaxation time.

Let us use this idea, at least formally, to generalize *Eq.* (2.4), i.e., moisture diffusion. Then, instead of *Eq.* (2.4) we have

$$\underline{f} + \tau_m \dot{\underline{f}} = -D_m \nabla m \tag{3.5}$$

and instead of *Eq.* (2.5)

$$\dot{m} + \tau_m \ddot{m} = D_m \nabla^2 m. \tag{3.6}$$

What is the physical meaning of this equation? Certainly the paradox of the infinite speed is removed, moisture transport is described by a hyperbolic equation, however, the physical mechanism behind it is still not clear, neither are the real values of τ_m.

We apply now a formal generalization of basic equations including the Dufour and Soret effects. First we introduce the relaxation time into the constitutive law. Then for fluxes i, we have

$$\underline{J}_i + \tau_{ij} \dot{\underline{J}}_j = -\alpha_{ij} \nabla C_j. \tag{3.7}$$

Substituting (3.7) into the conservation law, we obtain

$$\dot{C}_i + \tau_{ij}\ddot{C}_j = D_{ij}\nabla^2 C_j + \sigma_i + \tau_{ij}\dot{\sigma}_j. \tag{3.8}$$

In our case $i, j = 1, 2$ with $C_1 = m, C_2 = T$. The corresponding equations in these terms are the following.

(i) Constitutive laws

$$\begin{bmatrix} \underline{f} \\ \underline{q} \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ \tau_{21} & \tau_{22} \end{bmatrix} \begin{bmatrix} \dot{\underline{f}} \\ \dot{\underline{q}} \end{bmatrix} = - \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix} \begin{bmatrix} \nabla m \\ \nabla T \end{bmatrix}, \tag{3.9}$$

(ii) Governing equations

$$\begin{bmatrix} \dot{m} \\ \dot{T} \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ \tau_{21} & \tau_{22} \end{bmatrix} \begin{bmatrix} \ddot{m} \\ \ddot{T} \end{bmatrix} =$$

$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \begin{bmatrix} \nabla^2 m \\ \nabla^2 T \end{bmatrix} + \begin{bmatrix} \sigma_1 \\ \sigma_2 \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} \\ \tau_{21} & \tau_{22} \end{bmatrix} \begin{bmatrix} \dot{\sigma}_1 \\ \dot{\sigma}_2 \end{bmatrix}. \tag{3.10}$$

These are the formal results and some comments are in order. It is obvious that $\tau_{11} = \tau_m$ and $\tau_{22} = \tau_T$. The other two relaxation times $\tau_{12} = \tau_m^T$ and $\tau_{21} = \tau_T^m$ characterize coupling effects. Due to Onsager's reciprocal relations we may suppose

$$\tau_{12} = \tau_{21}. \tag{3.11}$$

Though there is total analogy between Fourier's heat conduction and Fick's moisture diffusion law, there are also basic differences between the two problems [7].

The first one is that heat conduction is in connection with the microstructure of a single material while moisture diffusion connects two materials (porous solid and fluid), and their macrostructure has a basic role. As a consequence, dealing with this process one has to take into account the conservation of mass and also inertia terms. Of course, this behavior is present during the coupled processes, too.

Another characteristic difference between heat conduction and the cross coupled heat and moisture diffusion is the following: In a heat conduction process, there is practically no temperature limitation. In the cross-coupled process there exist two limitations: freezing and evaporation of moisture. This means that also phase changes have to be considered. If the temperature is too low, the fluid freezes and the voids disappear; without porous material the whole problem becomes different. If the temperature is too high the fluid begins to evaporate, the pressure rises and after a while, the fluid disappears; without moisture the problem is again different. It is apparent that the temperature range of the cross-coupled problem is strictly limited. Of course, the whole argument is valid in the case of elastic motion.

4. Possible Reasons for the Non-Symmetry in Coupled Fields

Starting with the basic equations of conventional thermo-elasticity, after derivation, holding as basic functions temperature (T) and displacement (u_i) one gets the so-called generalized equation of motion and heat conduction:

$$\mu u_{i,jj} + (\mu + \lambda)\, u_{k,ki} = \rho \ddot{u}_i - \rho b_i - \beta T_{,i}, \tag{4.1}$$

$$T_{,ii} - \frac{\rho c}{k}\dot{T} - \beta T_0 \frac{1}{k}\dot{u}_{i,i} = 0. \tag{4.2}$$

Formally the same relations are valid in the case of hygro-elasticity. The unsymmetry in coupling is obvious. While the temperature field influences the displacement field through its gradient ($T_{,i}$) the influence of the displacement field on the temperature distribution is accomplished by the divergence and the time rate of the displacement ($\dot{u}_{i,i}$).

The question could be regarded from different points of view.

In the general equation of motion (4.1) the role of the temperature field is similar to the body force. (See the second and third terms on the right-hand side). In the general equation of heat conduction (4.2) the role of displacement divergence is similar to the temperature.

$$T_{,ii} = \left[\frac{\rho c}{k}T + T_0 \frac{\beta}{k} u_{i,j}\right]^{\cdot} \tag{4.3}$$

From another point of view the problem is similar to the constitutive equation of a viscous material, where the stress does not depend on the displacement gradient ($u_{i,j}$) as in the case of an elastic material, but on the velocity gradient ($\nu_{i,j}$). Recognition of this feature may lead to a possible approach to the problem. Rheological models give a possible handling of the phenomenon by using the generalized equations.

A possible approach to the reasons for the problem may rely on the physical background, i.e., the reversibility-irreversibility in connection with the changes of mechanical work to heat and vice versa. Another possibility, in connection with the previous remarks, is the structure of the material. While the displacement is related to the macrostructure of the material, heat conduction (change of temperature) involves the microstructure.

It is also possible that the law of heat conduction is the reason for the problem. Using the modified basic equation, which leads to a hyperbolic equation, one may get a better understanding of the unsymmetry. This consideration may lead to another type of coupled system which is closer to the symmetric one.

There are also several questions from a technical point of view. The role of time (time rate of displacement divergence) has been mentioned, but the speed of changes has not been dealt with. It is possible that in the case of low speed the time rate is negligible [3].

Another technical problem arises from the fact that mathematically the differentiation and integration are not reversible.

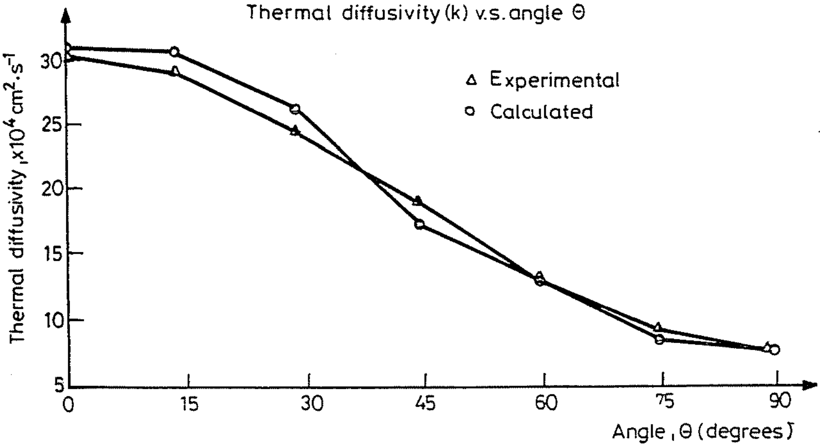

Fig. 2. Comparison of experimental and calculated values of thermal diffusivity for graphite-epoxy as a function of fiber orientation, at room temperature

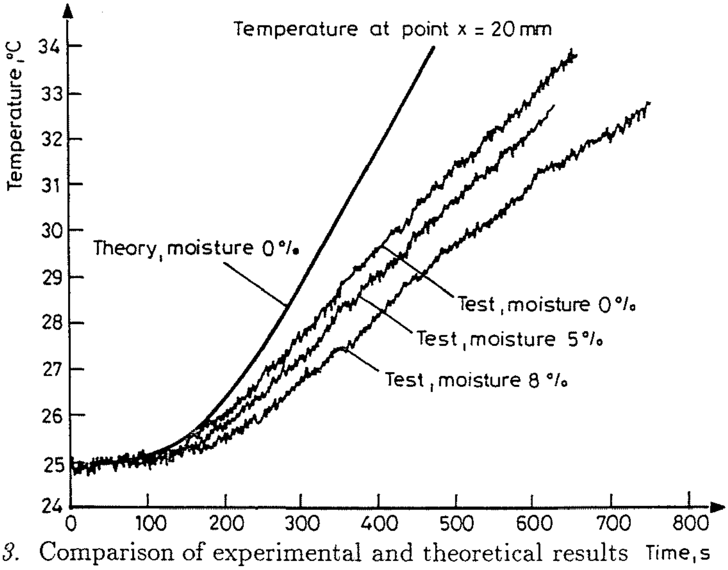

Fig. 3. Comparison of experimental and theoretical results
Temperature response 20 mm from a heated end

5. Application for Tailoring of Composite Materials

As an application of the equations introduced in the previous sections, they may be used for the tailoring of composites.

Considering the constitutive equations of anisotropic THE solid, the generalized constitutive law is recalled together with Fourier's heat conduction law and Fick's moisture transport relation:

$$\epsilon_{ij} = a_{ijkl}\sigma_{kl} + \alpha_{ij}^{m}\nabla m, \qquad q_i = -k_{ij}T_{,j} \qquad f_i = -(D_m)_{ij}m_{,j}. \tag{5.1}$$

Instead of the latter two equations, the coupled and modified relation based on the "second sound" phenomenon will be applied. For anisotropic THE materials, *Eq.* (2.7) becomes

$$J_{\alpha i} + \tau_{\alpha\beta ij}\dot{J}_{\beta j} = -d_{\alpha\beta ij}C_{\beta,j} \tag{5.2}$$

with

$$\alpha, \beta = 1, 2,$$
$$k, l, i, j = 1, 2, 3.$$

Here

$$J_{\alpha i} = \begin{bmatrix} f_i \\ q_i \end{bmatrix}, \quad \tau_{\alpha\beta ij} = \begin{bmatrix} (\tau_m)_{ij} & (\tau_m^T)_{ij} \\ (\tau_T^m)_{ij} & (\tau_T)_{ij} \end{bmatrix},$$

$$d_{\alpha\beta ij} = \begin{bmatrix} (d_m)_{ij} & (d_m^T)_{ij} \\ (d_T^m)_{ij} & k_{ij} \end{bmatrix}, \quad C_{\beta,j} = \begin{bmatrix} m_{,j} \\ T_{,j} \end{bmatrix}$$

are the extended matrices of flux, relaxation, diffusivity, and concentration gradients, respectively.

On the basis of parameters contained in the coefficients of *Eqs.* (5.1,2) listed in the Introduction, tailoring can be performed. As it was mentioned before, the number of required values can be reduced through various symmetry conditions. Most of the material properties are available in handbooks though some are not. As applications of the theory, some examples are presented [4, 7] in *Figs.* 2–5.

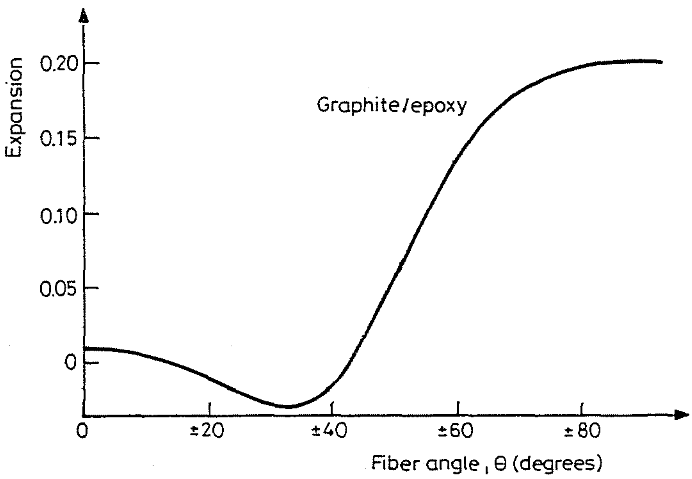

Fig. 4. Longitudinal CT/ME of Symmetric Balanced Laminate

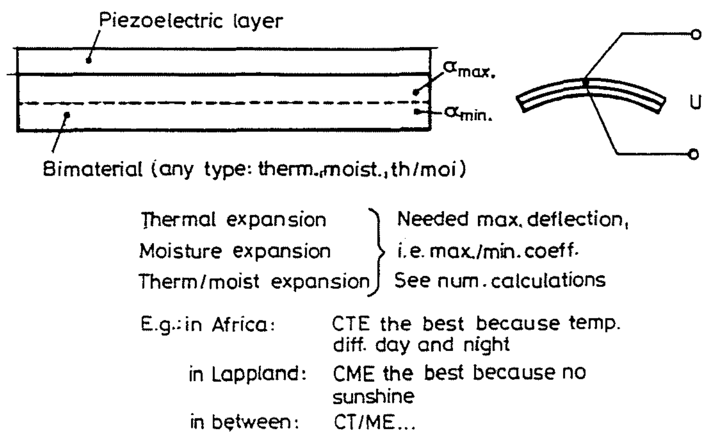

Fig. 5. Light-house energy supply

6. Conclusions

Onsager's reciprocal relations help to define the material properties for coupled fields, e.g., diffusivities and relaxation parameters. In the case of thermo-hygro materials, in the application of reciprocal relations some specialities have to be considered (see dimensions). We found a possible interpretation for the non-symmetry in the governing equations of coupled fields (see thermo-elastic coupling). With Onsager's relations we were able to obtain numerical values of coefficients for practical applications (see composite materials).

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