

Thermodiffusion as a superposition of processes

T. HOFFMANN (POZNAŃ)

IN THE PAPER the thermodiffusion process [1, 2, 3, 4] in a non-deformable medium is studied. It has been demonstrated that in a linear process of thermodiffusion the temperature and the chemical potential are the superposition of certain fields described by independent, classical equations of transport. Assuming that there are no chemical reactions on the boundary of the body, the initial-boundary conditions have been formulated for these fields.

W pracy bada się proces termodyfuzji [1, 2, 3, 4] w ośrodku nieodkształcalnym. Wykazano, że w liniowym procesie termodyfuzji temperatura oraz potencjał chemiczny są superpozycją pewnych pól opisywanych niezależnymi, klasycznymi równaniami transportu. Przy założeniu braku reakcji chemicznych na brzegu ciała sformułowano warunki początkowo-brzegowe dla tych pól.

В работе исследуется процесс термодиффузии [1, 2, 3, 4] в недеформируемой среде. Показано, что в линейном процессе термодиффузии температура и химический потенциал являются суперпозицией некоторых полей, описываемых независимыми, классическими уравнениями переноса. При предположении отсутствия химических реакций на границы тела, сформулированы начально-граничные условия для этих полей.

Introduction

THE TERM „thermodiffusion” became generally accepted in the theory of coupled fields as denoting the mutual influences of thermal processes and diffusion in the materials modelled as continuous media.

From the formal point of view the coupled fields are denoted by the coupled set of partial differential equations and the initial boundary conditions.

Equations of thermodiffusion were derived for the first time by J. C. PODSTRIGACZ [1] and it was W. NOWACKI who complemented this theory and gave some general theorems [2, 3, 4].

The technological significance of the considered processes is great in the field of surface treatment of materials as well as in the production of precision alloys for the electronic industry. In these technologies special protective atmospheres are used which provide for free diffusion. Chemical constitution of the atmosphere is chosen in regard to the elements emerging on the surface as a result of diffusion (e.g. in decarburization of steel the so-called humidified hydrogen $H_2 + H_2O$ is used). The role of the atmosphere is to collect these elements from the surface of the material and to prevent surface chemical reactions which would inhibit the diffusion process [5, 6] and deteriorate the quality of the treatment. The theoretical description [1, 2, 3, 4] accounts for the coupling with the elastic deformation field.

In this paper the subject of interest is the process of thermodiffusion where the deformability of material was neglected. An attempt has been undertaken to demonstrate

that in the linear thermodiffusion process, the temperature and the chemical potential are the superposition of certain processes described by the independent classical equations of transport. In other words, it occurs that the set of equations of thermodiffusion can be decoupled using linear transformation. The influence of this transformation on the initial and boundary conditions is also examined. The purpose of the paper is purely cognitive.

1. Basic equations

We assume the set of equations of thermodiffusion following W. NOWACKI [3], neglecting the deformation of the medium,

$$(1.1) \quad \begin{aligned} \Delta\theta &= a\partial_t\theta + b\partial_t\mu, \\ \Delta\mu &= c\partial_t\theta + d\partial_t\mu, \end{aligned}$$

where

$$\Delta = \sum_{i=1}^3 \frac{\partial^2}{\partial x_i^2}, \quad \partial_t = \frac{\partial}{\partial t},$$

θ — relative temperature of the material,

μ — chemical potential of the diffusing component,

a, b, c, d — material constants.

Let us assume that there exist the independent functions ξ, η such that

$$(1.2) \quad \begin{aligned} \theta &= \xi + \alpha\eta, \\ \mu &= \beta\xi + \eta, \end{aligned}$$

where α, β are the parameters independent of position and time which fulfil the condition of non-singularity of transformation:

$$(1.3) \quad 1 - \alpha\beta \neq 0.$$

The quantities ξ, η are the new representations of the state of a medium. The function ξ has the dimension of temperature, whereas η has the dimension of chemical potential.

After application of the transformation (1.2), the set (1.1) can be written down in the form

$$(1.4) \quad \begin{aligned} [\Delta\xi - (a + \beta b)\partial_t\xi] + \alpha \left[\Delta\eta - \left(a + \frac{b}{\alpha}\right)\partial_t\eta \right] &= 0, \\ \beta \left[\Delta\xi - \left(d + \frac{c}{\beta}\right)\partial_t\xi \right] + [\Delta\eta - (d + \alpha c)\partial_t\eta] &= 0. \end{aligned}$$

The parameters α, β of the transformation (1.2) are chosen so that they fulfil the equations

$$(1.5) \quad (a + \beta b) = \left(d + \frac{c}{\beta}\right), \quad \left(a + \frac{b}{\alpha}\right) = (d + \alpha c)$$

the solutions of which are

$$(1.6) \quad \beta = \frac{(d-a) \pm \sqrt{\delta}}{2b}, \quad \alpha = -\frac{(d-a) \pm \sqrt{\delta}}{2c},$$

where

$$\delta = (d-a)^2 + 4bc.$$

Among these solutions we shall choose

$$(1.7) \quad \alpha = -\frac{(d-a) - \sqrt{\delta}}{2c}, \quad \beta = \frac{(d-a) - \sqrt{\delta}}{2b}$$

which fulfill the condition (1.3)

Considering the above assertions we can find the coefficients in the set (1.4)

$$(1.8) \quad \begin{aligned} (a + \beta b) &= \left(d + \frac{c}{\beta} \right) = \frac{1}{2} [(a+d) - \sqrt{\delta}], \\ (d + \alpha c) &= \left(a + \frac{b}{\alpha} \right) = \frac{1}{2} [(a+d) + \sqrt{\delta}]. \end{aligned}$$

The set of Eq. (1.4) will be written down in a symbolic form:

$$(1.9) \quad \begin{aligned} P(\mathbf{x}, t) + \alpha R(\mathbf{x}, t) &= 0, \\ \beta P(\mathbf{x}, t) + R(\mathbf{x}, t) &= 0, \end{aligned}$$

where

$$\begin{aligned} P(\mathbf{x}, t) &= \Delta \xi - \frac{1}{2} [(a+d) - \sqrt{\delta}] \partial_t \xi, \\ R(\mathbf{x}, t) &= \Delta \eta - \frac{1}{2} [(a+d) + \sqrt{\delta}] \partial_t \eta. \end{aligned}$$

The set of equations (1.9) will be treated as an algebraic set of linear homogeneous equations for the unknowns P and R . According to the condition (1.3), this set always has trivial solutions ([7], p. 37). In this way we obtain two independent equations describing the functions ξ and η ,

$$(1.10) \quad \begin{aligned} \Delta \xi - \frac{1}{2} [(a+d) - \sqrt{\delta}] \partial_t \xi &= 0, \\ \Delta \eta - \frac{1}{2} [(a+d) + \sqrt{\delta}] \partial_t \eta &= 0. \end{aligned}$$

These are the classical equations of transport.

The question can be asked if the transformation (1.2) with the condition (1.3) is unique and if Eqs. (1.10) are equivalent to the primary set of equations.

Let us apply to the set (1.1) the classical method of decomposition by increasing the order of the equation. We shall obtain

$$(1.11) \quad \begin{aligned} \Delta \Delta \tau_i - (d+a) \Delta \partial_t \tau_i + (ad - cb) \partial_t^2 \tau_i &= 0, \quad i = 1, 2, \\ \tau_1 &= \theta, \quad \tau_2 = \mu. \end{aligned}$$

Each one of these equations can be displayed in the form

$$(1.12) \quad D_1 D_2 \tau_i = 0, \quad i = 1, 2,$$

where

$$D_1 = \left\{ \Delta - \frac{1}{2} [(a+b) + \sqrt{\delta}] \partial_i \right\},$$

$$D_2 = \left\{ \Delta - \frac{1}{2} [(a+b) - \sqrt{\delta}] \partial_i \right\}.$$

The operators D_1 and D_2 are commutative.

The above assertions fulfill the premises of the Boggio theorem [9]; therefore, according to the proposition of this theorem, the solutions of Eq. (1.11) have the form

$$(1.13) \quad \tau_i = \tau_i^I + \tau_i^{II}, \quad i = 1, 2,$$

where τ_i^I, τ_i^{II} have to satisfy the equations

$$(1.14) \quad D_1 \tau_i^I = 0,$$

$$D_2 \tau_i^{II} = 0.$$

This confirms the result of Eq. (1.10) because we can take

$$(1.15) \quad \theta^I = \xi, \quad \theta^{II} = \alpha\eta,$$

$$\mu^I = \beta\xi, \quad \mu^{II} = \eta.$$

The Boggio theorem confirms the uniqueness of the decomposition (1.2) and the equivalence of equations (1.10) to the set (1.1).

. Initial and boundary conditions

All the methods of decomposition of the sets of differential equations in the conjugate theories are submitted to further verification when applied to the initial boundary conditions. Frequently it happens that the decomposition method couples the boundary conditions, thus making the effective solution difficult.

Let us think over this problem in our case.

Assume that the initial conditions for temperature and chemical potential are given in the form

$$(2.1) \quad \theta(\mathbf{x}, 0) = \varphi(\mathbf{x}),$$

$$\mu(\mathbf{x}, 0) = \psi(\mathbf{x}).$$

According to the transformation (1.2) and (1.3), we shall easily find the initial conditions for the functions ξ and η

$$(2.2) \quad \xi(\mathbf{x}, 0) = \frac{1}{1 - \alpha\beta} [\varphi(\mathbf{x}) - \alpha\psi(\mathbf{x})],$$

$$\eta(\mathbf{x}, 0) = \frac{1}{1 - \alpha\beta} [-\beta\varphi(\mathbf{x}) + \psi(\mathbf{x})].$$

In the considerations on boundary conditions let us assume first that on the surfaces S of the solid body the exchange of mass and heat with the environment takes place. Let the environment be characterized by the given temperature θ_0 and the given chemical potential μ_0 which, according to Eqs. (1.2) and (1.3), can be expressed the given functions ξ_0, η_0 .

The chemical potential is a so-called universal thermodynamical function, i.e. it is continuous on the surface of discontinuity [8] if on this surface no chemical reactions take place.

Let us write down formally the classical conditions of the mass and heat exchange:

$$(2.3) \quad \left. \frac{\partial \theta}{\partial n} + h(\theta - \theta_0) \right|_S = 0, \\ \left. \frac{\partial \mu}{\partial n} + h'(\mu - \mu_0) \right|_S = 0,$$

where n — direction normal to the surface, h, h' — coefficients characterizing the surface.

We shall take into consideration the postulated continuity of the chemical potential on the surface S :

$$(2.4) \quad (\mu - \mu_0)|_S = 0.$$

Substituting the condition (2.4) to the condition (2.3)₂, we obtain

$$(2.5) \quad \left. \frac{\partial \mu}{\partial n} \right|_S = 0.$$

We shall display the conditions (2.4) and (2.5) in the representation ξ, η with the use of the transformation (1.2), (1.3)

$$(2.6) \quad \beta(\xi - \xi_0) = -(\eta - \eta_0)|_S, \\ \beta \frac{\partial \xi}{\partial n} = -\frac{\partial \eta}{\partial n} \Big|_S.$$

We shall apply the transformation (1.2) to the condition of heat exchange (2.3)₁, and then we shall use the conclusions (2.6) what will lead to

$$(2.7) \quad \left. \frac{\partial \xi}{\partial n} + h(\xi - \xi_0) \right|_S = 0, \\ \left. \frac{\partial \eta}{\partial n} + h(\eta - \eta_0) \right|_S = 0.$$

The formulae (2.7) are the boundary conditions of the so-called third kind for the functions ξ and η in the absence of chemical reaction on the surface of a body.

In the light of the condition (2.5), the boundary conditions of the second kind should have the form

$$(2.8) \quad \left. \frac{\partial \theta}{\partial n} \right|_S = f(t), \quad \left. \frac{\partial \mu}{\partial n} \right|_S = 0.$$

After applying the transformation (1.2), (1.3) to Eq. (2.8), we shall obtain the boundary conditions of the second kind for the functions ξ and η ,

$$(2.9) \quad \left. \frac{\partial \xi}{\partial n} \right|_s = (1 - \alpha\beta)^{-1} f(t),$$

$$\left. \frac{\partial \eta}{\partial n} \right|_s = -\beta(1 - \alpha\beta)^{-1} f(t).$$

If we assume the boundary conditions of the first kind for the temperature and chemical potential

$$(2.10) \quad \theta|_s = \theta_0,$$

$$\mu|_s = \mu_0$$

then, according to relations (1.2) and (1.3), they will have the form

$$(2.11) \quad \xi|_s = (1 - \alpha\beta)^{-1}(\theta_0 - \alpha\mu_0),$$

$$\eta|_s = (1 - \alpha\beta)^{-1}(-\beta\theta_0 + \mu_0).$$

The formulae (2.11) are the boundary conditions of the first kind for the functions ξ , η

3. Analysis of the obtained results

Linear transformation (1.2), (1.3) decouples the set of basic equations (1.1) into two independent classical equations of transport (1.10). The initial conditions of the problem can be imposed according to (2.2).

Owing to the assumption of lack of chemical reactions on the surface of the body, the boundary conditions of all the three kinds can be formulated according to the relations (2.7), (2.9), (2.11). The obtained results permit us to state that in the thermodiffusion process, in linear approximation, the temperature and the chemical potential are the superposition of certain independent elementary processes described by the functions ξ and η .

Formulation of the boundary conditions for these functions is related to the assumption of lack of chemical reactions on the boundary; however, this assumption is satisfied in numerous technological processes.

4. Final conclusions

In the light of the present paper the lack of a theory describing the influence of surface chemical reactions on the process of thermodiffusion becomes evident. Such a theory would probably allow for the formulation of a broader class of boundary conditions. Such a theory is not known to the author, however.

The obtained results can be useful in the description of real technological processes.

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TECHNICAL UNIVERSITY OF POZNAŃ.

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