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# Thermomechanics of dried materials

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THE THERMOMECHANICAL behaviour of fluid-saturated capillary-porous materials exposed to a drying process is examined in the paper. Basing on the balance equations of mass, momentum, energy and entropy and on the restrictions imposed on these equations by the thermodynamics of irreversible processes, one develops the differential equations describing the evolution of the drying body deformations, and the temperature and moisture concentration fields. Several periods of the drying process are distinguished and for these periods the respective models are proposed. The presented theory concerns an arbitrary technology of drying, but examples of boundary conditions are given for the convective means of drying, which is mostly employed in technology.

W pracy analizuje się zjawiska termomechaniczne związane z przebiegiem procesu suszenia zawilżonych materiałów kapilarno-porowatych. Opierając się na równaniach bilansu masy, pędu, energii i entropii oraz ograniczeniach, jakie nakłada na te równania termodynamika procesów nieodwracalnych, wyprowadza się równania różniczkowe opisujące ewolucję rozkładu deformacji ciała suszonego, jego temperatury i koncentracji zawartej w nim wilgoci w każdym punkcie pola. W procesie suszenia wyróżnia się pewne jego fazy, różniące się mechanizmem wymiany ciepła i masy. Dla tych wyróżnionych faz proponuje się odpowiednie modele suszenia. Przedstawiona teoria odnosi się do dowolnej techniki suszenia. Przy analizie warunków brzegowych główny nacisk położono na konwekcyjny sposób suszenia, który w praktyce jest najbardziej rozpowszechniony.

В работе анализируются термомеханические явления, связанные с ходом процесса сушки отсырелых капиллярно-пористых материалов. Базируя на уравнениях баланса массы, импульса, энергии и энтропии, а также на ограничениях, какие накладывает на эти уравнения термодинамика необратимых процессов, выводятся дифференциальные уравнения, описывающие эволюцию распределения деформации сушенного тела, его температуры и концентрации, содержавшейся в ним влажности в каждой точке поля. В процессе сушки различаются некоторые его фазы, отличающиеся механизмом теплообмена и массообмена. Для этих выделенных фаз предлагаются соответствующие модели сушки. Представленная теория относится к произвольной технике сушки. При анализе граничных условий главное внимание обращается на конвекционный способ сушки, который в практике является наиболее распространенным.

## Notation

| | |
|---|---|
| $\mathbf{x}_s[\mathrm{m}]$, $\mathbf{X}_s[\mathrm{m}]$ | position vectors, |
| $t[\mathrm{s}]$ | time, |
| $\mathbf{u}_s = (\mathbf{x}_s - \mathbf{X}_s)[\mathrm{m}]$ | displacement vector of the porous solid |
| $\mathbf{F}_s = \mathrm{Grad}\,\mathbf{x}_s(\mathbf{X}_s, t)[1]$ | deformation gradient, |
| $J = \det \mathbf{F}_s[1]$ | Jacobian, |
| $\mathbf{d}_s[1/\mathrm{s}]$ | strain rate tensor, |
| $\mathbf{E}_s[1]$ | Green strain tensor, |
| $\mathbf{v}_\alpha[\mathrm{m/s}]$ | velocity vector of the $\alpha$th constituent, |
| $\mathbf{V}[\mathrm{m/s}]$ | velocity vector of the interface, |
| $\mathscr{B}_0[\mathrm{m}^3]$ | body volume, |
| $\partial\mathscr{B}_0[\mathrm{m}^2]$ | body boundary surface, |
| $dv[\mathrm{m}^3]$ | volume element, |

| | |
|---|---|
| $da\,[\mathrm{m}^2]$ | surface element, |
| $\Phi_\alpha\,[1]$ | volume fraction of the αth constituent, |
| $\Phi\,[1]$ | porosity ratio, |
| $\varrho^t_\alpha\,[\mathrm{kg/m^3}]$ | true mass density of the αth constituent, |
| $\varrho_\alpha = \varrho^t_\alpha \Phi_\alpha\,[\mathrm{kg/m^3}]$ | bulk mass density of the αth constituent, |
| $\theta_\alpha = (\varrho_\alpha/\varrho_0)\,[1]$ | mass fraction of the αth constituent, |
| $\theta\,[1]$ | specific moisture content, |
| $\mathbf{b}_\alpha\,[\mathrm{N/kg}]$ | body force in the αth constituent, |
| $\mathbf{T}_\alpha\,[\mathrm{N/m^2}]$ | partial stress tensor of the αth constituent, |
| $\mathbf{S}\,[\mathrm{N/m}]$ | surface stress tensor, |
| $\mathbf{T}\,[\mathrm{N/m^2}]$ | total stress tensor, |
| $p_\alpha\,[\mathrm{N/m^2}]$ | true pressure of the αth constituent, |
| $P_\alpha = -p_\alpha \Phi_\alpha\,[\mathrm{N/m^2}]$ | bulk pressure of the αth constituent, |
| $u_\alpha\,[\mathrm{J/kg}]$ | specific internal energy of the αth constituent, |
| $s_\alpha\,[\mathrm{J/kg^\circ K}]$ | specific entropy of the αth constituent, |
| $\mu^{\mathrm{ch}}_\alpha\,[\mathrm{J/kg}]$ | chemical potential of the αth constituent, |
| $\mu^{\mathrm{cap}}_\alpha\,[\mathrm{J/kg}]$ | capillary potential of the αth constituent, |
| $\mu_\alpha = \mu^{\mathrm{ch}}_\alpha + \mu^{\mathrm{cap}}_\alpha\,[\mathrm{J/kg}]$ | thermodynamic potential of the αth constituent, |
| $U_\alpha,\ F_\alpha\,[\mathrm{J/m^3}]$ | internal energy, free energy, of the αth constituent, per unit bulk volume of the reference configuration, |
| $S_\alpha\,[\mathrm{J/m^3\ ^\circ K}]$ | entropy of the αth constituent per unit bulk volume of the reference configuration, |
| $\mathbf{q}_\alpha\,[\mathrm{W/m^2}]$ | heat flux vector of the αth constituent, |
| $\mathbf{q}^s\,[\mathrm{W/m}]$ | surface heat flux vector, |
| $\boldsymbol{\eta}_\alpha\,[\mathrm{kg/m^2\ s}]$ | mass flux vector of the αth constituent, |
| $T_\alpha\,[^\circ\mathrm{K}]$ | absolute temperature of the αth constituent, |
| $\vartheta_\alpha = T_\alpha - T_r\,[^\circ\mathrm{K}]$ | relative temperature of the αth constituent, |
| $l\,[\mathrm{J/kg}]$ | latent heat of evaporation, |
| $M\,[\mathrm{N/m^2}]$ | shear modulus for the porous solid, |
| $A\,[\mathrm{N/m^2}]$ | bulk modulus for the porous solid, |
| $\alpha^T_s\,[1/^\circ\mathrm{K}]$ | coefficient of linear thermal expansion of the saturated matrix, |
| $\alpha^m_s\,[1]$ | coefficient of linear swelling of the saturated matrix, |
| $A'\,[\mathrm{m^2/N}]$ | coefficient of expansion of the porous body by the penetrating moisture pressure, |
| $\alpha_T\,[\mathrm{W/m^{2\circ}K}]$ | coefficient of the convective heat transfer, |
| $\alpha_m\,[\mathrm{kg^2/Jms}]$ | coefficient of the convective mass transfer, |
| $c_{v\alpha}\,[\mathrm{J/m^{3\circ}K}]$ | specific heat of the αth constituent at constant volume per unit bulk volume, |
| $c_{p\alpha}\,[\mathrm{J/kg^\circ K}]$ | specific heat of the αth constituent at constant pressure per unit mass, |
| $\varrho^*_\alpha\,[1/\mathrm{s}]$ | production of αth constituent mass, |
| $m^*_\alpha\,[\mathrm{N/kg}]$ | production of αth constituent momentum, |
| $e^*_\alpha\,[\mathrm{J/kgs}]$ | production of αth constituent energy. |

## Subscripts

| | |
|---|---|
| 0 | perfectly dry body, |
| 1 | bound liquid, |
| 2 | free liquid, |
| 3 | humid air (gas), |
| $s$ | saturated matrix, |
| $f$ | fluid, |
| $g$ | gas, |
| $l$ | liquid, |
| $r$ | physical reference, |
| $R$ | geometrical reference. |

## 1. Introduction

A THERMODYNAMIC theory is developed to predict the thermomechanical behaviour of a fluid-saturated, capillary-porous body during the process of drying. Basing on the balance equations of mass, momentum, energy, and entropy which used to be employed in mixture theories [1, 2, 4, 7, 13, 15, 17, 18] and on the restrictions imposed on these equations by the thermodynamics of irreversible processes, [13, 36, 44, 49], one develops the differential equations describing the evolution of the dried body deformation and the temperature and moisture concentration fields.

The theory presented here deals with an arbitrary technology of drying and in this sense it is of a general character. But the analysis of boundary conditions is mainly accentuated for the convective means of drying which is mostly employed in technology.

This paper is a generalization and continuation of the author's earlier contribution [22]. The generalization consists in considering the phase transitions not only on the evaporation surface but also inside the whole body, what actually takes place in real processes. The continuation means here an extension of the previous theory to the so-called second period of drying. This period, called also the decreasing drying rate period, (see, e.g., [20, 33, 42]), was not considered in the paper [22]. In this period for some kinds of dried materials, the evaporation surface (surface of phase transitions) may recede from the boundary toward the inside of the dried body. In such a case the problem of heat and mass transfer is mathematically formulated as that with moving boundaries, which may be referred to as an example of the Stefan problem [26]. Therefore one considers here a moving evaporation surface which divides the medium into two regions for which the surface is a common boundary. The surface is regarded as a singular one at which some thermodynamic fields posses discontinuities. In this regard the considerations shall be mostly supported by the results presented in the paper [35] and in the monograph [21].

This study differs from other ones dealing with the same subject (see, e.g., [31, 47]) in some substantial questions. Firstly, one takes into consideration here the deformability of the dried material as a phenomenon coupled to the drying process. This phenomenon has been taken into account in the drying theory by LUCIK [32] and the author [22]. Secondly, the equations of heat and mass transfer are developed here basing on the fundamental balance equations and the restrictions implied on the constitutive equations by the entropy inequality. It leads, in fact, to a concept of heat and mass transfer equations other than those obtained by utilizing the Onsager principle. Thirdly, one analyses here in detail the particular periods of drying by performing equations and boundary conditions suitable for the given period. Thus we obtain here a drying theory which gives rise to mathematical modelling of the thermomechanics of the drying process in the whole time of its duration. This paper supposedly does not dwell on all the effects accompanying drying of fluid-saturated porous bodies. The problem is very complex and characterized by various phenomena. Only a theoretical model of drying is shown here which, to the author's mind, reveals the most substantial features of the real drying process. It was built basing on experimental data from the respective literature. The model alone requires also experimental verification and, in particular, an estimation of some material constants existing in the model.

## 2. Description of the medium

Referring to the knowledge of structure of dried materials, [20, 33, 42], we state that the medium in hand consists of the following constituents:

(i) an elastic porous matrix (skeleton of the medium),

(ii) a liquid bounded physically and chemically with the skeleton (cellular liquid); the kinematics of this constituent is the same as that of the skeleton,

(iii) a liquid bounded physically and mechanically with the skeleton (capillary liquid) having its own kinematics,

(iv) humid air contained in the medium in the form of bubbles having also its own kinematics.

Thus we shall consider a porous medium whose pores are filled up with a three-component mixture of the bounded liquid, free liquid, and gas. We assume the pores of the medium to be intercommunicating void spaces; thus there exists the possibility of migration of the moisture through the medium. The dimension of the pores is greater than the intermolecular distances (i.e. $10^{-8}$ cm) and smaller than the dimensions excluding the capillarity (i.e. $10^{-1}$ cm). Dried materials most commonly found, e.g., ceramics, have such dimensions of pores.

The peculiar constituents will be marked out with the indices $\alpha = 0, 1, 2, 3$ referring to the porous matrix, bounded liquid, free liquid, and gas, in that order.

According to the averaging procedure (see, e.g., [15, 41, 47, 48]) we assume that each constituent is characterized by the intrinsic volume average mass density (true mass density) $\varrho^t_\alpha$ and the bulk (partial) mass density $\varrho_\alpha$. They are related to each order by

$$\varrho_\alpha = \Phi_\alpha \varrho^t_\alpha, \tag{2.1}$$

where $\Phi_\alpha$ is the volume fraction representing the volume of the $\alpha$th constituent per unit volume of the medium as a whole.
Therefore

$$\sum_{\alpha=0}^{3} \Phi_\alpha = 1. \tag{2.2}$$

From here we state that the quantity

$$\Phi = 1 - \Phi_0 = \sum_{\alpha=1}^{3} \Phi_\alpha, \tag{2.3}$$

is the porosity ratio of the medium. Determination of the volume fractions is possible. The amount of bounded liquid can be determined by sorption and desorption isoterms analysis or by measuring changes of thermal or electrical conductivities. The amount of free fluid is determined by the permeability coefficient for a given porous material. The amount of gas in the medium can be determined by the weight, acoustics, X-rays or other methods.

We shall use in our study the notion of specific moisture content defined as

$$\theta = \frac{\varrho_1 + \varrho_2 + \varrho_3}{\varrho_0} = \theta_1 + \theta_2 + \theta_3, \quad \theta_\alpha = \frac{\varrho_\alpha}{\varrho_0}. \tag{2.4}$$

The mean velocities of the constituents obtained by utilizing the mass average operator, [15, 41], will be denoted by $\mathbf{v}_\alpha$, $\alpha = 0, 1, 2, 3$. According to the previous assumption, $\mathbf{v}_1 \equiv \mathbf{v}_0$.

The thermodynamic system in our consideration will be the interior of the body separated mentally from the medium by a regular and closed control surface fixed to the porous solid. The porous solid plays here the role of diathermous, open, and deformable "container" for the moisture. The moisture flux through the control surface is determined by

$$\boldsymbol{\eta}_\alpha = \varrho_\alpha(\mathbf{v}_\alpha - \mathbf{v}_0). \tag{2.5}$$

The change of constituent mass due to phase transition will be denoted by $\varrho^*_\alpha$, but $\varrho^*_0 = 0$. The partial stress tensor for the $\alpha$th constituent of the moisture is assumed to be isotropic, i.e.,

$$\mathbf{T}_\alpha = P_\alpha \mathbf{I} = -p_\alpha \Phi_\alpha \mathbf{I} \quad \text{for} \quad \alpha = 1, 2, 3, \tag{2.6}$$

where $p_\alpha$ denotes the true pressure of the $\alpha$th constituent and $\mathbf{I}$ is the unit second-order tensor.

## 3. Description of the drying model

A possibility of determining the drying process is provided by measuring the change in weight of the dried material. In this way the curve of drying is drawn up as it is seen in Fig. 1. This curve shows that the drying process consists of several periods which differ from one another in the mechanisms of heat and mass transfer. Generally, each drying process can be divided into the constant drying rate period (Period I) and the decreasing drying rate period (Period II).

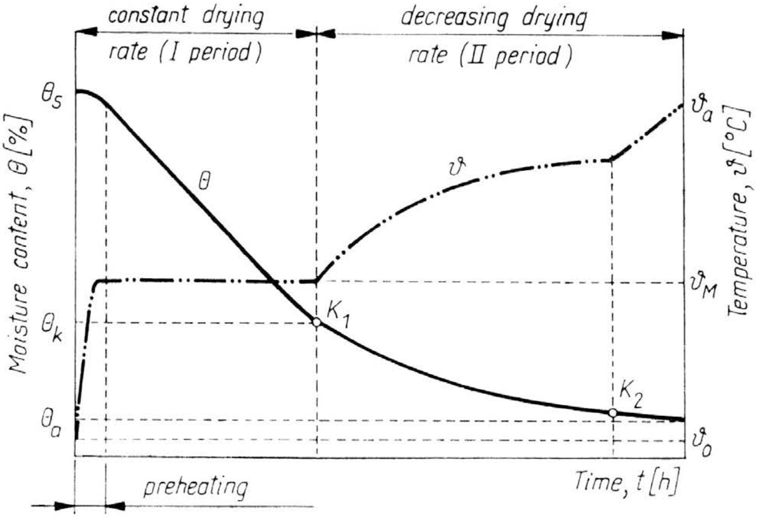

FIG. 1. Curve of drying of fluid saturated capillary-porous material.

In Period I the free liquid is removed. We take into consideration three important mechanisms in our model concerning Period I:

(i) the migration of moisture from the interior of the dried material out to the surface,

(ii) the evaporation of the moisture from the surface of the dried material,

(iii) the growth of gas bubbles inside the dried material. The gas bubbles are very small when the porous material is fully saturated, $\theta = \theta_s$. Because of the surface tension, they are stuck to the pore walls, [16]. In the course of drying the bubbles grow and finally reach the dimension of the capillary-pore. At this time the stream of liquid flowing from the interior out to the surface of the dried material breaks. We assume that at this moment Period I passes to Period II of drying. This occurs when the moisture content reaches the critical value $\theta = \theta_k$(1).

Two different mechanisms of drying are possible in Period II:

(i) the evaporation surface recedes from the boundary toward the inside for nonhygroscopic materials and gross pores, or

(ii) the evaporation of the physically and chemically bounded liquid proceeds from the pore walls in the whole pore space and, next, diffusion of the vapour toward the outside of the material takes place. This mechanism is referred to as hygroscopic materials.

The end of the drying process occurs when the moisture content reaches the equilibrium value with the surrounding atmosphere, $\theta = \theta_e$.

It is worth pointing out here that the temperature of a dried material increases quickly in the preheating period from the initial value $\vartheta = \vartheta_0$ to the wet-bulb temperature $\vartheta = \vartheta_M$; next it is kept fixed during Period I and increases to the value of the surrounding atmosphere $\vartheta = \vartheta_a$ at the end of Period II. All these mechanisms of heat and mass transfer mentioned above will be taken into consideration in this paper.

## 4. Balance equations for Period I of drying

This section contains a brief introduction to the balance equations appropriate for the drying theory in Period I or in Period II for the case of hygroscopic materials, i.e., when there is no singular surface inside the dried material.

Consider now a moving three-dimensional body $\mathcal{B}(t)$. Let us separate mentally from the body an arbitrary three-dimensional part $\mathcal{B}_0(t)$ bounded by a regular control surface $\partial\mathcal{B}_0(t)$ being fixed to the skeleton grains and oriented spatially by the outward directed unit normal vector $\mathbf{n}$, Fig. 2. We shall consider $\mathcal{B}_0(t)$ for the thermodynamic system. Thus the thermodynamic system is open, diathermic, continuous and moving with the velocity field $\mathbf{v}_0(\mathbf{x}_s, t)$.

The time derivative of a time-dependent measure of thermodynamic quantity $\Psi_\alpha(t)$ referred to the constituent $\alpha$ and having the volumed ensity $\psi_\alpha(\mathbf{x}_s, t)$ can be expressed as

$$(4.1) \qquad \frac{d^\alpha \Psi_\alpha(t)}{dt} = \int\limits_{\mathcal{B}_0(t)} [\psi_\alpha(\mathbf{x}_s, t)\,dv]^{\cdot} + \int\limits_{\partial\mathcal{B}_0(t)} \psi_\alpha(\mathbf{x}_s, t)[\mathbf{v}_\alpha(\mathbf{x}_s, t) - v_0(\mathbf{x}_s, t)] \cdot \mathbf{n}\,da.$$

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(1) For some materials the second critical point $K_2$ on the drying curve is distinguished. From this point strongly nonlinear reductions of drying rate take place.

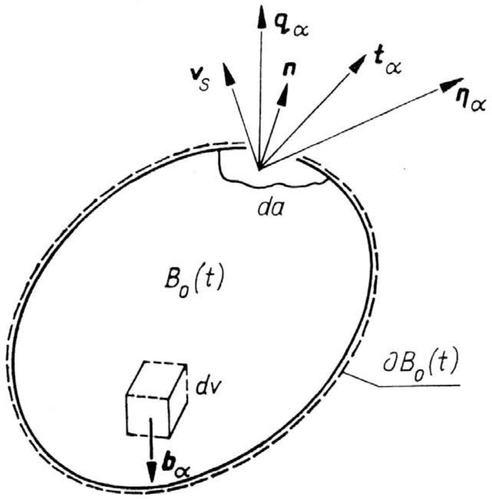

FIG. 2. Control volume for analysis of moisture flow through a porous body.

The first integral in Eq. (4.1) expresses time changes of $\Psi_\alpha(t)$ in the moving region $\mathscr{B}_0(t)$, the dot denotes the time derivative with convection velocity $\mathbf{v}_0(\mathbf{x}_s, t)$.

The second integral in Eq. (4.1) describes the changes of $\Psi\ (t)$ as a result of the net outword flow of the constituent $\alpha$ across the control surface.

Using the theorem of measure transport, [41],

$$\dot{\overline{dv}} = \operatorname{div} \mathbf{v}_0 \, dv, \tag{4.2}$$

and the divergence theorem, we rewrite Eq. (4.1) as follows:

$$\frac{d^\alpha \Psi_\alpha(t)}{dt} = \int\limits_{\mathscr{B}_0(t)} [\dot{\psi}_\alpha + \psi_\alpha \operatorname{div} \mathbf{v}_0 + \operatorname{div} \psi_\alpha(\mathbf{v}_\alpha - \mathbf{v}_0)] \, dv. \tag{4.3}$$

In continuum thermodynamics a general balance statement for a body $\mathscr{B}_0(t)$ is given in the form, [49],

$$\frac{d^\alpha \Psi_\alpha(t)}{dt} = \Lambda(\Psi_\alpha) + \mathscr{S}(\Psi_\alpha) + \mathscr{P}(\Psi_\alpha) + \mathscr{D}(\Psi_\alpha). \tag{4.4}$$

In Eq. (4.4) $\Lambda(\Psi_\alpha)$ is the efflux of $\Psi_\alpha$ through the boundary of the body having the following representation:

$$\Lambda(\Psi_\alpha) = \int\limits_{\partial \mathscr{B}_0(t)} \lambda_\alpha(n) \, da. \tag{4.5$_1$}$$

$\mathscr{S}(\Psi_\alpha)$ is the supply of $\Psi_\alpha$ in $\mathscr{B}_0(t)$,

$$\mathscr{S}(\Psi_\alpha) = \int\limits_{\mathscr{B}_0(t)} s_\alpha \, dv, \tag{4.5$_2$}$$

and $\mathscr{P}(\Psi_\alpha)$ is the production of $\Psi_\alpha$ in $\mathscr{B}_0(t)$,

$$\mathscr{P}(\Psi_\alpha) = \int\limits_{\mathscr{B}_0(t)} p_\alpha^* \, dv. \tag{4.5$_3$}$$

$\mathcal{D}(\Psi_\alpha)$ is a measure of long range interaction and is assumed in our considerations to be equal to zero.

We assume the flux principles

$$\lambda_\alpha(\mathbf{n}) = \boldsymbol{\lambda}_\alpha \cdot \mathbf{n}, \tag{4.6}$$

and apply the divergence theorem to rewrite the efflux $(4.5)_1$ as follows:

$$\Lambda(\Psi_\alpha) = \int\limits_{\mathcal{B}_0(t)} \operatorname{div} \boldsymbol{\lambda}_\alpha \, dv. \tag{4.7}$$

Thus the general balance equation (4.4) can be written in the local form

$$\dot{\psi}_\alpha + \psi_\alpha \operatorname{div} \mathbf{v}_0 = \operatorname{div}[\boldsymbol{\lambda}_\alpha - \psi_\alpha(\mathbf{v}_\alpha - \mathbf{v}_0)] + s_\alpha + p_\alpha^*. \tag{4.8}$$

Special equations of balance will be obtained using the notation introduced in Table 1, where $u_\alpha$ is the specific internal energy of the $\alpha$th constituent, $\mathbf{T}_\alpha$ is the partial Cauchy stress, $\mathring{\mathbf{q}}_\alpha$ is the heat flux vector into the $\alpha$th constituent through the surface $\partial\mathcal{B}_0(t)$.

**Table 1.**

| $\Psi_\alpha$ | $\psi_\alpha$ | $\lambda_\alpha$ | $s_\alpha$ | $p_\alpha^*$ |
|---|---|---|---|---|
| Mass | $\varrho_\alpha$ | $0$ | $0$ | $\varrho_\alpha \varrho_\alpha^*$ |
| Momentum | $\varrho_\alpha \mathbf{v}_\alpha$ | $\mathbf{T}_\alpha$ | $\varrho_\alpha \mathbf{b}_\alpha$ | $\varrho_\alpha \mathbf{m}_\alpha^*$ |
| Energy | $\varrho_\alpha\left(u_\alpha + \frac{1}{2}\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha\right)$ | $\mathbf{T}_\alpha \mathbf{v}_\alpha - \mathring{\mathbf{q}}_\alpha$ | $\varrho_\alpha(r_\alpha + \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha)$ | $\varrho_\alpha e_\alpha^*$ |

Because of the mass efflux through the surface $\partial\mathcal{B}_0(t)$, the heat flux $\mathring{q}_\alpha$ consists of $\mathbf{q}_\alpha$ as if there were no mass efflux and is diminished by the total heat transported by the mass efflux $\boldsymbol{\eta}_\alpha s_\alpha T_\alpha$, i.e.,

$$\mathring{\mathbf{q}}_\alpha = \mathbf{q}_\alpha - \boldsymbol{\eta}_\alpha s_\alpha T_\alpha, \tag{4.9}$$

where $\boldsymbol{\eta}_\alpha$, $s_\alpha$, $T_\alpha$ are the mass efflux, specific entropy, and absolute temperature of the $\alpha$th constituent, respectively. Further notations in Table 1 are: $\mathbf{b}_\alpha$ is the partial external body force density, $r_\alpha$ is the external heat supply density and $\varrho_\alpha^*$, $m_\alpha^*$ and $e_\alpha^*$ denote, respectively, the internal mass, momentum and energy production densities due to the exchange of these thermodynamic quantities between the constituents.

The equations of balance of mass, momentum and energy read as

$$\dot{\varrho}_\alpha + \varrho_\alpha \operatorname{div} \mathbf{v}_0 = -\operatorname{div} \boldsymbol{\eta}_\alpha + \varrho_\alpha \varrho_\alpha^*, \tag{4.10}$$

$$\dot{\overline{\varrho_\alpha \mathbf{v}_\alpha}} + \varrho_\alpha \mathbf{v}_\alpha \operatorname{div} \mathbf{v}_0 = \operatorname{div}[\mathbf{T}_\alpha - \varrho_\alpha \mathbf{v}_\alpha \otimes (\mathbf{v}_\alpha - \mathbf{v}_0)] + \varrho_\alpha \mathbf{b}_\alpha + \varrho_\alpha \mathbf{m}_\alpha^*, \tag{4.11}$$

$$\begin{aligned} \varrho_\alpha \dot{\overline{\left(u_\alpha + \frac{1}{2}\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha\right)}} + \varrho_\alpha\left(u_\alpha + \frac{1}{2}\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha\right) \operatorname{div} \mathbf{v}_0 = \operatorname{div}\Big[\mathbf{T}_\alpha \mathbf{v}_\alpha - \mathring{\mathbf{q}}_\alpha \\ - \varrho_\alpha\left(u_\alpha + \frac{1}{2}\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha\right)(\mathbf{v}_\alpha - \mathbf{v}_0)\Big] + \varrho_\alpha(r_\alpha + \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha) + \varrho_\alpha e_\alpha^*, \end{aligned} \tag{4.12}$$

where

$$\sum_{\alpha=0}^{3} \varrho_\alpha \varrho_\alpha^* = 0, \quad \sum_{\alpha=0}^{3} \varrho_\alpha \mathbf{m}_\alpha^* = 0, \quad \sum_{\alpha=0}^{3} \varrho_\alpha e_\alpha^* = 0 \tag{4.13}$$

must hold.

We rearrange Eqs. (4.10) to (4.12) writing these equations separately for the porous body and for the moisture contained in pores. Thus we have for $\alpha = 0$

$$\dot{\varrho}_0 + \varrho_0 \operatorname{div} v_0 = 0, \tag*{(4.10)$_1$}$$

$$\varrho_0 \dot{\mathbf{v}}_0 = \operatorname{div} \mathbf{T}_0 + \varrho_0 \mathbf{b}_0 + \varrho_0 \mathbf{m}_0^*, \tag*{(4.11)$_1$}$$

$$\varrho_0 \dot{u}_0 = \operatorname{tr} \mathbf{T}_0 \mathbf{L}_0 - \operatorname{div} \mathbf{q}_0 + \varrho_0 r_0 + \varrho_0 \hat{e}_0, \tag*{(4.12)$_1$}$$

where

$$\mathbf{L}_0 = \operatorname{grad} \mathbf{v}_0 \tag*{(4.13)$_1$}$$

is the velocity gradient of the porous body, and for $\alpha = 1, 2, 3$

$$\varrho_0 \theta_\alpha = -\operatorname{div} \boldsymbol{\eta}_\alpha' + \dot{\varrho}_\alpha \varrho_\alpha^*, \tag*{(4.10)$_2$}$$

$$\mathbf{v}_\alpha' + \frac{1}{2} \varrho_\alpha^* (\mathbf{v}_\alpha - \mathbf{v}_0) = -\operatorname{grad} \mu_\alpha + \mathbf{b}_\alpha + \hat{\mathbf{m}}_\alpha, \tag*{(4.11)$_2$}$$

$$\varrho_0 \dot{\hat{u}}_\alpha = P_\alpha \operatorname{div} \mathbf{v}_0 + \varrho_0 \mu_\alpha' \dot{\theta}_\alpha - \operatorname{div} \mathbf{q}_\alpha + \varrho_\alpha r_\alpha + \varrho_\alpha (\hat{e} - \varrho_\alpha^* \mu_\alpha) - \boldsymbol{\eta}_\alpha \cdot \hat{\mathbf{m}}_\alpha, \tag*{(4.12)$_2$}$$

where $\hat{u}_\alpha = \theta_\alpha u_\alpha$ is the specific internal energy of the $\alpha$th constituent referred to the mass of the porous solid, and

$$\mu_\alpha = u_\alpha - s_\alpha T_\alpha - \frac{1}{\varrho_\alpha} P_\alpha \tag{4.14}$$

is the thermodynamic potential of the $\alpha$th constituent. As it is seen, in Eq. (4.11)$_2$ we have made the moisture potential gradient responsible for the moisture motion. The new internal momentum and energy supply densities $\hat{\mathbf{m}}_\alpha$ and $\hat{e}_\alpha$ for $\alpha = 1, 2, 3$ are related to the old ones by

$$\hat{\mathbf{m}}_\alpha = \mathbf{m}_\alpha^* + \operatorname{grad} \mu_\alpha + \frac{1}{\varrho_\alpha} \operatorname{grad} P_\alpha - \frac{1}{2} \varrho_\alpha^* (\mathbf{v}_\alpha + \mathbf{v}_0), \tag{4.15}$$

$$\hat{e} = e_\alpha^* + \varrho_\alpha \mathbf{v}_0 \cdot \mathbf{v}_0 / 2 - \mathbf{m}_\alpha^* \cdot \mathbf{v}_0, \tag{4.16}$$

and must satisfy the conservation principles

$$\varrho_0 \mathbf{m}_0^* + \sum_{\alpha=1}^{3} \varrho_\alpha \hat{\mathbf{m}}_\alpha = 0 \quad \text{and} \quad \sum_{\alpha-0}^{3} \varrho_\alpha \hat{e} = 0. \tag{4.17}$$

In Eq. (4.11)$_2$ $\mathbf{v}_\alpha'$ denotes the acceleration of the $\alpha$th constituent for $\alpha = 1, 2, 3$.

We introduce now the equation of balance of entropy for the medium as a whole. If $s_\alpha$ denotes the entropy density for the $\alpha$th constituent, then

$$S = \int_{\mathscr{B}_0(t)} \sum_{\alpha=0}^{3} \varrho_\alpha s_\alpha \, dv \tag{4.18}$$

defines the total entropy for the medium. Its time changes read

$$(4.19)\qquad \frac{dS}{dt} = \int\limits_{\mathscr{B}_0(t)} \sum_{\alpha=0}^{3} \left(\dot{\overline{\varrho_\alpha s_\alpha}} + \varrho_\alpha s_\alpha \operatorname{div} \mathbf{v}_0 + \operatorname{div} s_\alpha \boldsymbol{\eta}_\alpha\right) dv.$$

The total entropy consists of a part $S_e$ that can be exchanged with the ambient medium and a part $S_i$ that can be produced inside the body. In agreement with the Clausius–Duhem postulate, the rate of changes of these entropies must satisfy the inequality

$$(4.20)\qquad \frac{dS_i}{dt} = \frac{d}{dt}(S - S_e) \geqslant 0.$$

Since the processes close to the equilibrium state are considered here, then the entropy exchanged with the ambient medium is assumed to be equal to the whole nonmechanical power exchanged with the ambient medium being referred to the absolute temperature, i.e.

$$(4.21)\qquad \frac{dS_e}{dt} = \sum_{\alpha=0}^{3} \left( - \int\limits_{\partial\mathscr{B}_0(t)} \frac{\mathring{\mathbf{q}}_\alpha}{T_\alpha} \cdot \mathbf{n}\, da + \int\limits_{\mathscr{B}_0(t)} \frac{\varrho_\alpha r_\alpha}{T_\alpha}\, dv \right).$$

Using Eqs. (4.19) and (4.21), we can write the local form of the inequality (4.20) as

$$(4.22)\qquad \sum_{\alpha=0}^{3} \left( \varrho_0 \dot{\hat{s}}_\alpha + \operatorname{div} \frac{\mathbf{q}_\alpha}{T_\alpha} - \frac{\varrho_\alpha r_\alpha}{T_\alpha} \right) \geqslant 0,$$

where $\hat{s}_\alpha = \theta_\alpha s_\alpha$ is the specific entropy of the $\alpha$th constituent referred to the mass of the porous solid. It follows from Eqs. $(4.12)_{1,2}$ and (4.22) by elimination of $(\operatorname{div}\mathbf{q}_\alpha - \varrho_\alpha r_\alpha)$ that

$$(4.23)\qquad \varrho_0 \dot{s} + \sum_{\alpha=0}^{3} \frac{1}{T_\alpha} \Bigg[ -\varrho_0 \dot{\hat{u}}_\alpha + \operatorname{tr} \mathbf{T}_\alpha \mathbf{L}_0 + \varrho_0 \mu_\alpha \dot{\theta}_\alpha - \frac{\mathbf{q}_\alpha}{T_\alpha} \cdot \operatorname{grad} T_\alpha$$
$$- \boldsymbol{\eta}_\alpha \cdot \hat{\mathbf{m}}_\alpha + \varrho_\alpha (\hat{e}_\alpha - \varrho_\alpha^* \mu_\alpha) \Bigg] \geqslant 0,$$

where $s = \sum\limits_{\alpha=0}^{3} \hat{s}_\alpha$ is the total entropy of the medium referred to the mass of the porous solid.

We shall use the inequality (4.23) to draw some conclusions concerning the constitutive relations and, in particular, the heat and mass transport equations.

## 5. Constitutive relations for dried materials

The deformations of dried materials are caused by both humidity and temperature action. They are not usually due to mechanical forces except in some particular cases of drying as wringing or centrifuging. Drying processes, however, are always accompanied by the internal mechanical forces inducing the drying stresses. These arise as a result of nonhomogeneous distributions of the moisture content and temperature. When these parameters are constant in the whole body, the drying stresses do not appear.

Now we shall derive the constitutive relations allowing, among others, the determination of drying stresses. The description of a nonequilibrium state is provided by the adoption of the principle of local state (see e.g. [50]) which recognizes that each of the independent thermodynamic properties $\psi_\alpha$ of the equilibrium end-states must now be replaced by an instantaneous field $\psi_\alpha(\mathbf{x}_s, t)$. Furthermore, the principle of local state asserts that the continuous system can be thought of as a collection of elementary (open) subsystems each of which undergoes a quasi-static irreversible process, and that the fundamental equilibrium equations of state remain valid locally and instantaneously. The principle of local equilibrium state is justified for its application to quasi-static processes, i.e., when the gradients of intensive functions or the differences between intensive constituent parameters of a multicomponent (or multiphase) system are small and when they change their local values in a sufficiently long period of time in comparison to the relaxation time.

In such a situation the Gibbs equation can be assumed to be valid. For the medium at hand this equation reads

$$\varrho_0 \dot{s} = \sum_{\alpha=0}^{3} \frac{1}{T_\alpha} [\varrho_0 \dot{\hat{u}}_\alpha - \mathrm{tr}\,\mathbf{T}_\alpha \mathbf{L}_0 - \varrho_0 \mu_\alpha \theta_\alpha]. \tag{5.1}$$

Substituting Eq. (5.1) into the inequality (4.23), we obtain a residual inequality of the form

$$\sum_{\alpha=0}^{3} \left[ \frac{1}{T_\alpha} \varrho_\alpha (\hat{e}_\alpha - \varrho_\alpha^* \mu_\alpha) - \sum_{\alpha=0}^{3} \frac{1}{T_\alpha} \left( \frac{\mathbf{q}_\alpha}{T_\alpha} \cdot \mathrm{grad}\, T_\alpha + \boldsymbol{\eta}_\alpha \cdot \dot{\mathbf{m}}_\alpha \right) \right] \geqslant 0. \tag{5.2}$$

The first sum in the inequality (5.2) expresses the entropy production due to an exchange of heat and mass between the constituents. The second sum in the inequality (5.2) performs the entropy production due to conduction of heat down the temperature gradient and due to the flow of moisture while there exists resistance of motion (e.g. viscosity).

As the individual sums in the expressions (5.4) have different tensorial representations, they ought to be positive defined independently, i.e.,

$$\begin{gathered} -\sum_{\alpha=0}^{3} \left[ \frac{1}{T_\alpha} \varrho_\alpha (\hat{e}_\alpha - \varrho_\alpha^* \mu_\alpha)(T_\alpha - T) + \varrho_\alpha \varrho_\alpha^* (\mu_\alpha - \mu) \right] \geqslant 0, \\ -\sum_{\alpha=0}^{3} \frac{1}{T_\alpha} \left[ \frac{q_\alpha}{T_\alpha} \cdot \mathrm{grad}\, T_\alpha + \boldsymbol{\eta}_\alpha \cdot \mathbf{m}_\alpha \right] \geqslant 0, \end{gathered} \tag{5.3}$$

where $T$ and $\mu$ are the full equilibrium temperature and the full equilibrium moisture potential, i.e., the temperature and the moisture potential the whole system would have had after a sufficient lapse of time when isolated. It is known (see, e.g., [12, 43]) that in any equilibrium state the peculiar temperatures and the chemical potentials for mixture constituents must be equal to each other. Temperature $T$ and potential $\mu$ can be defined here, for example, as

$$(5.4)\qquad T \overset{\mathrm{df}}{=} \Big(\sum_{\alpha=0}^{3} T_\alpha \hat{s}_\alpha\Big) \Big/ \sum_{\alpha=0}^{3} \hat{s}_\alpha, \qquad \mu \overset{\mathrm{df}}{=} \Big(\sum_{\alpha=0}^{3} \mu_\alpha \theta_\alpha\Big) \Big/ \sum_{\alpha=1}^{3} \hat{\theta}_\alpha.$$

DUNWOODY and MÜLLER [11] suggest other possibilities of defining the mean temperature for the mixture.

Assuming the inequalities (5.3) to be positive defined quadratic forms, we obtain the following rate equations:

(i) the rate of heat alteration of the $\alpha$th constituent due to heat exchange between the constituents

$$(5.5)_1\qquad \frac{1}{T_\alpha}\varrho_\alpha(\hat{e}_\alpha - \varrho^*_\alpha \mu_\alpha) = -\Lambda^T_\alpha(T_\alpha - T) - \Lambda^m_\alpha(\mu_\alpha - \mu),$$

with $\Lambda^m_0 \equiv 0$;

(ii) the rate of mass alteration of the $\alpha$th constituent due to phase transitions between the constituents

$$(5.5)_2\qquad \varrho_\alpha \varrho^*_\alpha = -\Gamma^T_\alpha(T_\alpha - T) - \Gamma^m_\alpha(\mu_\alpha - \mu),$$

with $\Gamma^T_0 \equiv 0$ and $\Gamma^m_0 \equiv 0$;

(iii) the rate of heat conduction through the $\alpha$th constituent

$$(5.5)_3\qquad \mathbf{q}_\alpha / T_\alpha = -\lambda^T_\alpha \operatorname{grad} T_\alpha - \lambda^m_\alpha \boldsymbol{\eta}_\alpha;$$

(iv) the rate of internal momentum supply

$$(5.5)_4\qquad \hat{\mathbf{m}} = -\gamma^T_\alpha \operatorname{grad} T_\alpha - \gamma^m_\alpha \boldsymbol{\eta}_\alpha.$$

The coefficients appearing in the relations (5.5) must satisfy the following (Silvester) criteria:

$$(5.6)\qquad \begin{aligned} \Lambda^T_\alpha &\geqslant 0, \quad \Lambda^T_\alpha \Gamma^m_\alpha \geqslant (\Lambda^m_\alpha + \Gamma^T_\alpha)^2/4, \\ \lambda^T_\alpha &\geqslant 0, \quad \lambda^T_\alpha \gamma^m_\alpha \geqslant (\lambda^m_\alpha + \gamma^T_\alpha)^2/4. \end{aligned}$$

To fulfil the criteria (5.6) for each possible process, some additional restrictions have to be imposed on the transport coefficients, namely, the symmetry, [22],

$$(5.7)\qquad \Lambda^m_\alpha = \Gamma^T_\alpha \quad \text{and} \quad \lambda^m_\alpha = \gamma^T_\alpha.$$

In many cases these coefficients can be assumed to be equal to zero (when neglecting for example the Dufour effect). Generally, they depend on the parameters of state.

The heat flow in moving in pore-space moisture is caused both by conduction and by convection. Assuming $\lambda^T_\alpha = \lambda_\alpha / T_\alpha$ and $-\lambda^m_\alpha = s_\alpha = c^m_{p\alpha}\vartheta_\alpha / T_\alpha$, where $c^m_{p\alpha}$ denotes the specific heat of the $\alpha$th constituent at constant pressure and $\vartheta_\alpha = T_\alpha - T_r$ is the relative temperature of the $\alpha$th constituent, we obtain from Eq. $(5.5)_3$ a generalized equation for heat flux suitable for filtration problems:

$$(5.8)\qquad \mathbf{q}_\alpha = -\lambda_\alpha \operatorname{grad} \vartheta_\alpha + c^m_{p\alpha}\vartheta_\alpha \boldsymbol{\eta}_\alpha, \qquad \lambda_\alpha \geqslant 0.$$

The second term in (5.8) describes the heat convected by the moisture. If it there wasn't any relative motion through the porous matrix, Eq. (5.8) would be reduced to the known Fourier rate equation.

Substituting the right hand side of Eq. $(5.5)_4$ into the equation of motion $(4.11)_2$, one obtains the following form of moisture transport equation for $\alpha = 2$ and 3:

$$(5.9)\qquad \overset{\prime}{\mathbf{v}}_\alpha + \gamma^*_\alpha(\mathbf{v}_\alpha - \mathbf{v}_0) = -\operatorname{grad}\mu_\alpha + \mathbf{b}_\alpha - \gamma^T_\alpha \operatorname{grad} T_\alpha,$$

where $\gamma^*_\alpha = \varrho_\alpha \gamma^m_\alpha + \varrho^*_\alpha/2$. In most cases of drying (except perhaps centrifuging), the acceleration $\overset{\prime}{\mathbf{v}}_\alpha$ can be taken as negligibly small. Then, it is convenient to write the moisture transport equation in the form of the moisture flux

$$(5.10)\qquad \boldsymbol{\eta}_\alpha = -\gamma_\alpha(\operatorname{grad}\mu_\alpha - \mathbf{b}_\alpha) - \gamma^{*T}_\alpha \operatorname{grad} T_\alpha,$$

where $\gamma_\alpha = 1/(\gamma^m_\alpha + \varrho^*_\alpha/2\varrho_\alpha)$, $\gamma^{*T}_\alpha = \gamma^T_\alpha \gamma_\alpha$. Such a form of moisture transport equation together with the mass balance equation $(4.10)_2$ leads to the thermodiffusion differential equation describing moisture distribution. We see that in the case of moisture potentials being equal to gravitational potentials, the first term on the r.h.s. disappears and the mass flux is due to the temperature gradient (thermodiffusion).

Now we come back to Gibbs' equation (5.1) which helps us to establish some physical relations. Note that $s = \sum_{\alpha=0}^{3} \hat{s}_\alpha$ $\left(\text{or } \dot{s} = \sum_{\alpha=0}^{3} \dot{\hat{s}}_\alpha\right)$ and therefore we can make on the basis of Eq. (5.1) the following identity:

$$(5.11)\qquad \dot{\hat{s}}_\alpha = \frac{1}{T_\alpha}\left[\dot{\hat{u}}_\alpha - \frac{1}{\varrho_0} \operatorname{tr} \mathbf{T}_\alpha \mathbf{L}_0 - \mu_\alpha Q_\alpha\right].$$

At this point we make an assumption that the temperature of the porous matrix $T_0$ is equal to the temperature of the bound liquid $T_1$ all the time during the course of drying. Such an assumption is justified by the fact that both these constituents move together all the time. Moreover, it is sensible to treat the porous matrix and the bound liquid as one whole. The reason for that is that the wet matrix has usually quite different properties than the dry one. Therefore we will henceforth speak of three (not four) constituents: saturated skeleton marked off by the index $s$, free liquid 2, and gas (humid air) 3. Thus we have the following Gibbs equations concerning the respective constituents:

$$(5.12)_1\qquad \dot{u}_s = \frac{1}{\varrho_s} \operatorname{tr} \mathbf{T}_s \mathbf{d}_s + \dot{s}_s T_s + \mu_1 \dot{\theta}_1,$$

for the saturated skeleton, $\alpha = s =$ "0" + "1", and

$$(5.12)_2\qquad \dot{\hat{u}}_\alpha = -\frac{1}{\varrho_0} p_\alpha \phi_\alpha \operatorname{div} v_s + \dot{s}_\alpha T_\alpha + \mu_\alpha \dot{\theta}_\alpha,$$

for $\alpha = 2$ and 3, where $u_s \equiv u_0 + \theta_1 u_1$, $s_s \equiv s_0 + \theta s_1$, $\mathbf{T}_s = \mathbf{T}_0 + P_1 \mathbf{I}$, $\mathbf{v}_0 = \mathbf{v}_1 = \mathbf{v}_s$, and

$$(5.13)\qquad \mathbf{d}_s = \frac{1}{2}\left(\operatorname{grad}\mathbf{v}_s + (\operatorname{grad}\mathbf{v}_s)^T\right)$$

denotes the strain rate tensor of the saturated skeleton.

Note that the deformation of the moist body is determined here by the deformation of the saturated matrix. It makes it possible to relate Gibbs' equation (5.12) to the reference configuration of the porous matrix and write

$$(5.14)\qquad \begin{aligned} \dot{U}_s &= \operatorname{tr} \mathbf{T}^R_s \dot{\mathbf{E}}_s + \dot{S}_s T_s + \mu_1 \dot{\Theta}_1 &&\text{for}\quad \alpha = s,\\ \dot{U}_\alpha &= -p_\alpha \dot{E}_{\dot{\alpha}} + \dot{S}_\alpha T_\alpha + \mu_\alpha \dot{\Theta}_\alpha &&\text{for}\quad \alpha = 2, 3, \end{aligned}$$

where

$$U_\alpha = \varrho_0^R \hat{u}_\alpha, \quad S_\alpha = \varrho_0^R \hat{s}_\alpha, \quad \Theta_\alpha = \varrho_0^R \theta_\alpha, \quad \Phi_\alpha^R = \Phi_\alpha J \quad \text{and} \quad \varrho_0^R = \varrho_0 J$$

are: internal energy, entropy, mass, and volume fraction of the $\alpha$th constituent, all per unit volume of the porous body reference configuration, and $J = \det F_s$ is the determinant of the deformation gradient $F_s = \text{Grad}\, \mathbf{x}_s(X_s, t)$. Furthermore

$$(5.15)_1 \qquad \mathbf{T}_s^R = J\mathbf{F}_s^{-1}\mathbf{T}_s(F_s^{-1})^T$$

is the second Piola–Kirchhoff stress tensor,

$$(5.15)_2 \qquad \dot{\mathbf{E}}_s = \mathbf{F}_s \mathbf{d}_s \mathbf{F}_s^{-1}$$

is the time derivative of the Green strain tensor $\mathbf{E}_s$, and

$$(5.15)_3 \qquad \dot{E}_\alpha \overset{\text{df}}{=} \Phi_\alpha^R \operatorname{div} \mathbf{v}_0$$

expresses the time alteration of the whole porous body volume caused by the pressure of the $\alpha$th constituent.

We shall assume that the thermodynamic state of an individual constituent will be known if $\mathbf{E}_s$, $T_s$ and $\Theta_1$ for $\alpha = s$ and $E_\alpha$, $T_\alpha$, $\Theta_\alpha$ for $\alpha = 2, 3$ are known. For thermal processes it is convenient to express the Gibbs identities (5.14) with the help of the free energy Helmholtz function

$$(5.16) \qquad F_\alpha \overset{\text{df}}{=} U_\alpha - S_\alpha T_\alpha$$

to obtain

$$(5.17)_1 \qquad \dot{F}_s = \operatorname{tr} \mathbf{T}_s^R \dot{\mathbf{E}}_s - S_s \dot{T}_s + \mu_1 \dot{\Theta}_1 \qquad \text{for} \quad \alpha = s,$$

$$(5.17)_2 \qquad \dot{F}_\alpha = -p_\alpha \dot{E}_\alpha - S_\alpha \dot{T}_\alpha + \mu_\alpha \dot{\Theta}_\alpha \qquad \text{for} \quad \alpha = 2, 3,$$

where

$$(5.18)_1 \qquad F_s = F_s(\mathbf{E}_s, T_s, \Theta_1) \qquad \text{for} \quad \alpha = s,$$

and

$$(5.18)_2 \qquad F_\alpha = F_\alpha(E_\alpha, T_\alpha, \Theta_\alpha) \qquad \text{for} \quad \alpha = 2, 3.$$

In order that the function (5.18) satisfy Gibbs' equation (5.17), it is necessary and sufficient that

$$(5.19)_1 \qquad S_s = -\left(\frac{\partial F_s}{\partial T_s}\right)_{\mathbf{E}_s, \Theta_1},$$

$$(5.19)_2 \qquad \mathbf{T}_s^R = \left(\frac{\partial F_s}{\partial \mathbf{E}_s}\right)_{T_s, \Theta_1},$$

$$(5.19)_3 \qquad \mu_1 = \left(\frac{\partial F_s}{\partial \Theta_1}\right)_{\mathbf{E}_s, T_s},$$

for $\alpha = s$ and

$$(5.19)_4 \qquad p_\alpha = -\left(\frac{\partial F_\alpha}{\partial E_\alpha}\right)_{T_\alpha, \Theta_\alpha},$$

$$S_\alpha = -\left(\frac{\partial F_\alpha}{\partial T_\alpha}\right)_{E_\alpha, \Theta_\alpha}, \tag{5.19$_5$}$$

$$\mu_\alpha = \left(\frac{\partial F_\alpha}{\partial \theta_\alpha}\right)_{E_\alpha, T_\alpha}, \tag{5.19$_6$}$$

for $\alpha = 2, 3$. These are the equations of state.

Basing on the tensor representation theorem, we write the stress-strain relation as follows (see, e.g., [46]):

$$\mathbf{T}_s^R = \varphi_1 \mathbf{I} + \varphi_2 \mathbf{E}_s + \varphi_3 \operatorname{tr} \mathbf{E}_s \mathbf{E}_s, \tag{5.20}$$

where $\varphi_k$, $k = 1, 2, 3$ are the material constants. We must remember that the deformation of a porous body consists of deformations of the matrix material and of deformations of the pore voids. In the absence of external mechanical forces, these deformations can be induced by the thermal expansion and by swelling of the solid matrix. The swelling is due to the presence of a second constituent (moisture) dispersed within the solid matrix (which belongs to the skeleton structure). COWIN [8, 9], ascertains that there are at least three ways by which the second constituent can cause the solid matrix to swell. The first way is by changing the concentration of the second constituent at constant specific volume, an example of which is the absorption of water by a microporous solid. The second way is by changing the specific volume of the second constituent at constant concentration.

Examples of this second way include soil heaving due to freezing of internal water, and the swelling induced by the thermal expansion of small, distributed gas bubbles within the solid matrix. The third way is simply a combination of the first two. An example here is the drying of most microporous materials where a change in phase of the second constituent from liquid to gas accompanies the process.

Thus the material constants depend on the temperature $T_s$, moisture content $\Theta_1$ and, in general, on the strains. For isotropic material

$$\varphi_k = \varphi_k(\mathrm{I}_E, \mathrm{II}_E, \mathrm{III}_E, T_s, \Theta_1), \quad k = 1, 2, 3 \tag{5.20$_1$}$$

where $\mathrm{I}_E, \mathrm{II}_E, \mathrm{III}_E$ are the invariants of the symmetric Green strain tensor $\mathbf{E}_s$.

For small deformations the term $\operatorname{tr}\mathbf{E}_s\mathbf{E}_s$ in Eq. (5.20) is a second order small quantity, and the difference between the Cauchy stress tensor $\mathbf{T}_s$ and the Piola–Kirchhoff stress tensor $\mathbf{T}_s^R$ is negligibly small so that one can approximate the stress-strain relation with a linear form with respect to strains. It is easy to state that for such a linear form $\varphi_1 = \psi_1 + \psi_2 \operatorname{tr} \mathbf{E}_s$ where the material constants now depend only on temperature and moisture content. For zero moisture content and isothermic processes $\psi_1$ ought to be equal to zero and the stress-strain relations become the familiar Hooke's law. Therefore we identify $\varphi_2 = 2M$, with $M$ being the shear modulus and $\psi_2 = A$ being the bulk modulus of the volumetric deformation for the fluid-saturated porous body. The linear stress-strain relation has then the form

$$\mathbf{T}_s = (\psi_1 + A \operatorname{tr} \mathbf{E}_s)\mathbf{I} + 2M\mathbf{E}_s. \tag{5.21}$$

Consider the situation when the total stress in the wet medium as a whole is equal to zero, i.e., $\mathbf{T} = \mathbf{T}_s + \sum_{\alpha=2}^{3} P_\alpha \mathbf{I} = 0$. Then the deviatoric components of the stress in the saturated solid matrix are equal to zero and its spherical part is equal to the partial pressure of the gas and free fluid constituents, i.e., $\mathbf{T}_s \cdot \mathbf{I} = -3 \sum\limits_{\alpha=2}^{3} P_\alpha$. Deformations of the saturated solid matrix then occur as a result of thermal expansion, swelling and compression by the free liquid and gas

$$(5.22) \qquad (\operatorname{tr}\mathbf{E}_s)_{\mathbf{T}=0} = 3\alpha_s^T \vartheta_s + 3\alpha_s^m \theta_1 + 3A' \sum_{\alpha=2}^{3} P_\alpha,$$

where $\alpha_s^T$ and $\alpha_s^m$ are the coefficients of linear thermal expansion and linear swelling for the saturated solid matrix, and $A'$ is a coefficient measuring the volume deformations of the moist body caused by both free liquid and gas in pores. Carrying out a mental experiment it is easy to state that an increase of the real pore pressure must cause an increase of the porous body volume, and therefore $A' \leqslant 0$, as $P_\alpha = -p_\alpha \Phi_\alpha \leqslant 0$.

In order to make this discussion more specific, let us quote an example of wood described by COWIN [8, 9]. "The internal liquid in wood is classified as either liquid that is free and liquid that is bound. The free liquid can move freely between the pores of the wood and its movement does not involve changes in the overall volume of the wood. On the other hand, the movement of the liquid designated as bound does involve changes in the volume of the wood. When the moisture content of wood is progressively reduced, the moisture content at which the cell walls are completely saturated, that is to say all the bound water is retained but no water exists in the cell cavities (no free water), is called the fiber saturation point. For wood the fiber saturation point represents about 30% moisture content. The fiber saturation point is generally considered to be the moisture content below which the physical and mechanical properties of wood begin to change as a function of moisture content".

In contrary to Cowin's statement, we have assumed in the present paper that the free liquid can also involve the overall volume deformations of the porous body but only through its pore pressure.

Basing on the above statements, we determine $\psi_1$ in Eq. (5.21) and write the linear stress-strain relation in the form

$$(5.23) \qquad \mathbf{T}_s = 2M\mathbf{E}_s + \Big[A \operatorname{tr}\mathbf{E}_s - \varkappa_s^T \vartheta_s - \varkappa_s^m \theta_1 - \varkappa_s^p \sum_{\alpha=2}^{3} P_\alpha\Big]\mathbf{I},$$

where

$$\varkappa_s^T = (2M+3A)\alpha_s^T, \quad \varkappa_s^m = (2M+3A)\alpha_s^m \quad \text{and} \quad \varkappa_s^p = 1+(2M+3A)A'.$$

Assuming the free energy functions for the individual constituents to be quadratic forms with respect to its arguments, we find the following shapes for partial entropy of the saturated skeleton:

$$(5.24)_1 \qquad S_s = \int_{T_{sr}}^{T_s} \frac{c_{vs}}{T_s}\, dT_s + \varkappa_s^T \operatorname{tr}\mathbf{E}_s + b_s^T \theta_1,$$

for the potential of the bound liquid

$$(5.24)_2 \qquad \mu_1 = (-b_s^T \vartheta_s - \varkappa_s^m \operatorname{tr} \mathbf{E}_s + b_s^m \theta_1)/\varrho_0,$$

and the partial entropies, constituent pressures, and the moisture potentials for $\alpha = 2$ and 3:

$$(5.24)_3 \qquad S_\alpha = \int_{T_{\alpha r}}^{T_\alpha} \frac{c_{v\alpha}}{T_\alpha} dT_\alpha + a_\alpha^T E_\alpha + b_\alpha^T \theta_\alpha,$$

$$(5.24)_4 \qquad p_\alpha = a_\alpha^T \vartheta_\alpha - a_\alpha^E E_\alpha + a_\alpha^m \theta_\alpha,$$

$$(5.24)_5 \qquad \mu_\alpha = (-b_\alpha^T \vartheta_\alpha - a_\alpha^m E_\alpha + b_\alpha^m \theta_\alpha)/\varrho_0.$$

The unknown coefficients $a_\alpha^T$, $a_\alpha^E$ and $a_\alpha^m$ determine the change of the constituent pressure (measurable quantity) by: change of temperature at constant $E_\alpha$ and $\theta_\alpha$, change of volume fraction at constant $T_\alpha$ and $\theta_\alpha$, change of constituent content at constant $T_\alpha$ and $E_\alpha$, in that order. The coefficient $c_{v\alpha}$ is the specific heat of the $\alpha$th constituent at constant volume per unit bulk volume, and the coefficient $b_\alpha^T/\varrho_0$ is a meassure of specific entropy of the $\alpha$th constituent (see [51], p. 115). By phase transitions $b_\alpha^T/\varrho_0$ may express the latent heat referred to the transition temperature (see [33] p. 112). The coefficient $b_\alpha^m/\varrho_0$ expresses a density of the moisture potential. Below is an example of how $b_\alpha^m$ can be determined in the case when $\mu_\alpha$ plays a role of capillary potential.

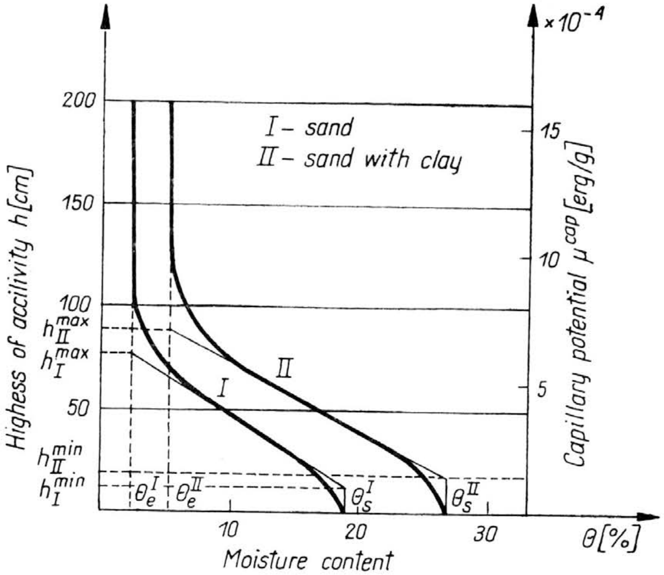

FIG. 3. Capillary potential versus moisture content.

Figure 3, which is redrawn from LYKOV [33], shows the height of acclivity of moisture in a sand sample. The lower boundary surface of the sample is immersed in water which, due to capillary forces, is hovered toward the top. Due to different dimensions of the capillary-pores, the height of acclivity varies in individual capillary-pores (lower in capillaries having a larger cross-section and higher in smaller ones). Thus the moisture distribution varies with height. Conversely, we can say that the height of wetting depends on the moisture content (maximal wetting is for $h_\alpha$ equal to 0). The capillary potential is defined as (see [33] p. 65)

$$\mu_\alpha^{\mathrm{cap}} = -p_\alpha^\sigma/\varrho_\alpha^t = [h_\alpha^{\max} - h_\alpha(\theta_\alpha)]g = b_\alpha^m \theta_\alpha, \tag{5.25}$$

where $p_\alpha^\sigma$ denotes the capillary pressure, $\varrho_\alpha^t$ true mass density, $h_\alpha^{\max}$ maximal height of acclivity, $h_\alpha(\theta_\alpha)$ height adequate to the moisture content $\theta_\alpha$, $g$ is the gravitational acceleration, and (see Fig. 3) $b_\alpha^m = (h_\alpha^{\max} - h_\alpha^{\min})/(\theta_\alpha^s - \theta_\alpha^e)$. Here $\theta_\alpha^s$ denotes the saturation humidity, i.e., maximal value of $\theta_\alpha$ in a given condition of wetting, and $\theta_\alpha^e$ is a minimum value of $\theta_\alpha$ (practically equal to zero) called equilibrium humidity.

Thus, knowing the moisture content in a given point of the medium, we can determine the capillary potential in this point.

The semi-empirical Leverett function (see [40] p. 47) gives also a possibility to determine $b_\alpha^m$.

The potential $\mu_\alpha$ is a quantity responsible for the transport and phase transitions of the $\alpha$-th constituent. Indeed, it consists of the chemical potential $\mu_\alpha^{\mathrm{ch}}$ and (say) capillary potential $\mu_\alpha^{\mathrm{cap}}$

$$\mu_\alpha = \mu_\alpha^{\mathrm{ch}} + \mu_\alpha^{\mathrm{cap}}. \tag{5.26}$$

The chemical potential $\mu_\alpha^{\mathrm{ch}} = u_\alpha - s_\alpha T_\alpha + p_\alpha^e/\varrho_\alpha^t$ is responsible for the phase transition, and the capillary potential $\mu_\alpha^{\mathrm{cep}} = -p_\alpha^\sigma/\varrho_\alpha^t$ is responsible for the transport of the moisture. Such a decomposition of the potential $\mu_\alpha$ is possible due to splitting of the pore pressure into the equilibrium pressure $p_\alpha^e$, i.e., the pressure the moisture would have if there were no any surface tension on the interfaces, and the additional (capillary) pressure $p_\alpha^\sigma$ caused by the surface tension (see [43]), i.e.,

$$p_\alpha^t = p_\alpha^e - p_\alpha^\sigma. \tag{5.27}$$

In general, the pressures $p_1^t, p_2^t, p_3^t$ differ from each other. The difference between $p_2^t$ and $p_3^t$ results from the surface tension on the bubble surfaces. The difference between $p_2^t$ and $p_1^t$ (wedging pressure) is due to the attraction of the bound liquid by the solid (see [33], p. 31).

The formulae (5.24), however, do not distinguish chemical and capillary potentials or quilibrium and additional pressures but describe the total values of these quantities expressed by the parameters of state. Specification of the constants appearing in these relations must be carried out each time, depending on the phase of the drying process as the mechanisms of heat and mass transfer in several periods of drying are different.

## 6. Final set of equations

Now we put together the basic equations of the theory. We do not deal any more with special cases of drying where the inertia force has a meaning (e.g., centrifuging), but with the drying that occurs as a thermal process.

From the mechanics point of view we must differentiate two groups of drying materials: those which suffer the main deformation in the first period of drying (e.g., clay), and those which do that in the second one (wood, coal, charcoal) (see [33] p. 185). The first group can be termed as colloidal bodies, and the second one as capillary-porous bodies.

*As for the moist colloidal bodies* (elastic gels), one states (see [33] p. 7) that they change strongly their dimensions together with the change of moisture content. Therefore we do not differentiate here between the bound and the free liquid and assume the phase transition to take place at the boundary surface (not inside of the body). Thus we consider the colloidal bodies as a moist matrix the drying of which can be described by the following set of equations:

(i) mechanical equilibrium

$$\operatorname{div}\mathbf{T}_s+\varrho_s\mathbf{b} = 0, \qquad \varrho_s = \varrho_0(1+\theta), \tag{6.1}$$

(ii) physical relations

$$\begin{aligned} \mathbf{T}_s &= 2M\mathbf{E}_s+(A\operatorname{tr}\mathbf{E}_s-\varkappa_s^T\vartheta-\varkappa_s^m\theta)\mathbf{I}, \\ \mu &= (-b^T\vartheta-a^m\operatorname{tr}\mathbf{E}_s+b^m\theta)/\varrho_0, \end{aligned} \tag{6.2}$$

(iii) geometrical relations

$$\mathbf{E}_s = \frac{1}{2}\left(\operatorname{grad}\mathbf{u}_s+(\operatorname{grad}\mathbf{u}_s)^T\right), \tag{6.3}$$

where $\mathbf{u}_s$ denotes the displacement vector of the dried body.

(iv) moisture mass balance equation

$$\varrho_0\dot{\theta} = -\operatorname{div}\boldsymbol{\eta}, \tag{6.4}$$

(v) balance of energy (heat)

$$c_{vs}\dot{\vartheta}+T(\varkappa^T\operatorname{tr}\dot{\mathbf{E}}_s+b^T\dot{\theta}) = -\operatorname{div}\mathbf{q}_s+\varrho_s r_s, \tag{6.5}$$

(vi) moisture transport equation

$$\boldsymbol{\eta} = -\gamma(\operatorname{grad}\mu-\mathbf{b})-\gamma^T\operatorname{grad}\vartheta, \tag{6.6}$$

(vii) heat transport equation

$$\mathbf{q}_s = -\lambda\operatorname{grad}\vartheta+c_{ps}^m\vartheta\eta. \tag{6.7}$$

The number of equations can be reduced if the physical relations are substituted into the mechanical equilibrium equations and the equations of balance of mass and energy are combined with the moisture and heat transport equations. Thus we obtain

$$\begin{gathered} M\nabla^2\mathbf{u}_s+\left(M+A-\varkappa_s^m\frac{a^m}{b^m}\right)\operatorname{grad}\operatorname{div}\mathbf{u}_s-\left(\varkappa_s^T+\varkappa_s^m\frac{b^T}{b^m}\right)\operatorname{grad}\vartheta-\varkappa_s^m\frac{\varrho_0}{b^m}\operatorname{grad}\mu+\varrho_s\mathbf{b} = 0, \\ \frac{\gamma}{\varrho_0}\nabla^2\mu = \frac{\varrho_0}{b^m}\dot{\mu}+\frac{b^T}{b^m}\dot{\vartheta}+\frac{a^m}{b^m}\operatorname{div}\mathbf{u}_s, \\ \lambda\nabla^2\vartheta = T_r\varrho_0\frac{b^T}{b^m}\dot{\mu}+\left(c_{vs}+T_r\frac{(b^T)^2}{b^m}\right)\dot{\vartheta}+T_r\left(\varkappa^T+b^T\frac{a^m}{b^m}\right)\operatorname{div}\dot{\mathbf{u}}_s. \end{gathered} \tag{6.8}$$

This is the set of linearized equations with the unknowns: $\mathbf{u}_s$, $\vartheta$ and $\mu$. For a univocal character of these equations the initial and boundary conditions must be added.

The initial values determine the values $\mathbf{u}_s$, $\vartheta$ and $\mu$ at $t = 0$. Among the number of boundary conditions, there are those describing the heat and mass transfer at the boundary

$\partial\mathscr{B}$, e.g., for convective drying they are:

$$(6.9)\qquad \alpha_T(\vartheta_a-\vartheta|_{\partial\mathscr{B}}) = -\lambda\operatorname{grad}\vartheta|_{\partial\mathscr{B}}\cdot\mathbf{n}-l\gamma\operatorname{grad}\mu|_{\partial\mathscr{B}}\cdot\mathbf{n},$$

$$\alpha_m(\mu_a-\mu|_{\partial\mathscr{B}}) = -\gamma\operatorname{grad}\mu|_{\partial\mathscr{B}}\cdot\mathbf{n},$$

where $\alpha_T$ and $\alpha_m$ are the convective heat and mass-transfer coefficients, $\vartheta_a$ and $\mu_a$ denote the temperature and the transfer potential of the surrounding atmosphere, and $l$ is the latent heat of vaporization.

*In the case of capillary-porous bodies* the evaporation of moisture occurs in two stages: first the free liquid and next the bound liquid is evaporized. The deformation and the temperature of a dried material during the first stage (I period) can be taken to be invariable. The differential equations governing the drying process in this stage reduce themselves to mass transfer equations. We then have

(i) moisture mass balance equations

$$(6.10)_1\qquad \varrho_0\dot{\theta}_\alpha = -\operatorname{div}\eta_\alpha+\varrho_\alpha\varrho^*_\alpha,\qquad \alpha = 2,3,$$

(ii) moisture transport equation

$$(6.10)_2\qquad \boldsymbol{\eta}_\alpha = -\gamma_\alpha(\operatorname{grad}\mu_\alpha-\mathbf{b}_\alpha),\qquad \alpha = 2,3,$$

(iii) moisture phase transition rule

$$(6.10)_3\qquad \varrho_\alpha\varrho^*_\alpha = -\Gamma^m_\alpha(\mu_\alpha-\mu),\qquad \alpha = 2,3,$$

(iv) moisture potential

$$(6.10)_4\qquad \mu_\alpha = c_\alpha+b_\alpha\theta_\alpha,\qquad \alpha = 2,3,$$

where

$$b_\alpha = b^m_\alpha/\varrho_0,\qquad c_\alpha = -(b^T_\alpha\vartheta_M+a^m_\alpha E_\alpha)/\varrho_0 \cong \text{const}.$$

and $\vartheta_M$ is the wet-bulb temperature.

The differential equation describing the moisture mass transfer can be expressed by the moisture content or by the moisture potential. Using the latter quantity we have

$$(6.11)\qquad \frac{\varrho_0}{b_\alpha}\dot{\mu}_\alpha = \gamma_\alpha\nabla^2\mu_\alpha-\Gamma^m_\alpha(\mu_\alpha-\mu),\qquad \alpha = 2,3.$$

The boundary condition determining the mass transfer between the dried material and the surrounding atmosphere has a form similar to Eq. $(6.9)_2$. Note that because $\varrho_2\varrho^*_2+\varrho_3\varrho^*_3 = 0$, we find on the basis of Eq. $(6.10)_3$

$$(6.12)\qquad \mu = \frac{\sum\limits_{\alpha=2}^{3}\Gamma^m_\alpha\mu_\alpha}{\sum\limits_{\alpha=2}^{3}\Gamma^m_\alpha}.$$

The differential equations governing the drying process in the second stage (Period II) are more complex since the temperature and the deformations of the dried material do not remain constant. We shall consider first a material with small pores, i.e., not having an evaporation surface inside the body. The free liquid is assumed to be absent in this stage and the drying involves here the removal of the bound liquid. This liquid is first evaporated inside the body and next, as a vapour, moves toward the outside of the body.

As the inertia forces are neglected, it is convenient to write the equation of mechanical equilibrium for the medium as a whole:

$$\operatorname{div}\mathbf{T}+\varrho\mathbf{b} = \varrho_3^*\boldsymbol{\eta}_3 \cong 0, \tag{6.13}$$

where $\mathbf{T} = \mathbf{T}_s+P_3\mathbf{I}$ is the total stress tensor and $\varrho = \varrho_s+\varrho_3 \cong \varrho_s$ is the mass density of the medium as a whole. The total stress tensor can be expressed on the basis of Eq. (5.23) as

$$\mathbf{T} = 2M\mathbf{E}_s+[A\operatorname{tr}\mathbf{E}_s-\varkappa_s^T\vartheta_s-\varkappa_s^m\theta_1-(\varkappa_s^p-1)P_3]\mathbf{I}. \tag{6.14}$$

The physical relation for the pore pressure is given by Eq. $(5.24)_4$. As the vapour fills now the whole pore space, we can assume $\phi_3 \cong$ const and write Eq. $(5.24)_4$ as follows:

$$P_3 = -\overline{a}_3^T\vartheta_3+\overline{a}_3^E\operatorname{tr}\mathbf{E}_s-\overline{a}_3^m\theta_3, \tag{6.15}$$

where

$$\overline{a}_3^T = a_3^T\phi_3, \qquad \overline{a}_3^E = a_3^E(\phi_3)^2, \qquad \overline{a}_3^m = a_3^m\phi_3$$

and in place of $E_3$ we substitute $E_3 = \phi_3 \operatorname{tr} \mathbf{E}_s$.

Mass transition determines the mass balance equations

$$\begin{aligned} \varrho_0\dot{\theta}_1 &= \varrho_1\varrho_1^*, \\ \varrho_0\dot{\theta}_3 &= -\operatorname{div}\eta_3+\varrho_3\overset{*}{\varrho}_3, \qquad \varrho_1\varrho_1^*+\varrho_3\varrho_3^* = 0 \end{aligned} \tag{6.16}$$

and both the mass transition rule $(5.5)_2$ and the mass transport rule (5.10) for $\alpha = 3$.

The heat transfer is determined by the energy balance equations reduced to

$$c_{vs}\dot{\vartheta}_s+T_s(\varkappa_s^T\operatorname{tr}\mathbf{E}_s+b_s^T\dot{\theta}_1) = -\operatorname{div}\mathbf{q}_s+\varrho_s r_s+\varrho_0\hat{e}_0+\varrho_1(\hat{e}_1-\varrho_1^*\mu_1), \tag{6.17$_1$}$$

and

$$c_{v3}\dot{\vartheta}_3+T_3(a_\alpha^T\phi_3\operatorname{tr}\mathbf{E}_s+b_3^T\dot{\theta}_3) = -\operatorname{div}\mathbf{q}_3+\varrho_3 r_3+\varrho_3(\hat{e}_3-\varrho_3^*\mu_3)-\boldsymbol{\eta}_3\cdot\hat{\mathbf{m}}_3 \tag{6.17$_2$}$$

and by the heat transition rule $(5.5)_1$ and heat transport rule (5.8). The interaction force $\hat{\mathbf{m}}_3$ is determined by Eq. $(5.5)_4$.

To complete the set of equations the physical relation for the moisture potential $(5.24)_2$ and $(5.24)_5$ for $\alpha = 3$ must be added. After neglecting some coupling effects similar to that of the Dufour one, the final linearized set of differential equations describing the heat and mass transfer and the deformations of dried material coupled with it, takes the form

$$\begin{aligned} &M\nabla^2\mathbf{u}_s+(M+\overline{A})\operatorname{grad}\operatorname{div}\mathbf{u}_s-\overline{\varkappa}_s^T\operatorname{grad}v_s-\overline{\varkappa}_3^T\operatorname{grad}v_3-\overline{\varkappa}_s^m\operatorname{grad}\mu_1-\overline{\varkappa}_3^m\operatorname{grad}\mu_3+\varrho\mathbf{b} = 0, \\ &0 = \frac{\varrho_0}{b_s^m}(\varrho_0\dot{\mu}_1+b_s^T\dot{\vartheta}_s+\varkappa_s^m\operatorname{div}\dot{\mathbf{u}}_s)+\Gamma^m(\mu_1-\mu_3), \\ &\gamma_3\nabla^2\mu_3 = \frac{\varrho_0}{b_3^m}(\varrho_0\dot{\mu}_3+b_3^T\dot{\vartheta}_3+a_3^m\phi_3\operatorname{div}\dot{\mathbf{u}}_s)-\Gamma^m(\mu_1-\mu_3), \\ &\lambda_s\nabla^2\vartheta_s+\varrho_s r_s = \overline{c}_{vs}\dot{\vartheta}_s+T_r\overline{\varkappa}_s^T\operatorname{div}\mathbf{u}_s+\overline{b}_s^T\dot{\mu}_1+\Lambda^T(\vartheta_s-\vartheta_3), \\ &\lambda_3\nabla^2\vartheta_3+\varrho_3 r_3 = c_{v3}\dot{\vartheta}_3+T_r\overline{a}_3^T\phi_3\operatorname{div}\mathbf{u}_s+\overline{b}_3^T\dot{\mu}_3-\Lambda^T(\vartheta_s-\vartheta_3), \end{aligned} \tag{6.18}$$

where

$$\overline{A} = A-(\varkappa_s^m)^2/b_s^m-\phi_3^2(\varkappa_s^p-1)(a_3^E-a_3^m)^2/b_3^m,$$

$$\begin{aligned} \bar{\varkappa}_s^T &= \varkappa_s^T + \varkappa_s^m b_s^T / b_s^m, & \bar{\varkappa}_3^T &= -\phi_3(\varkappa_s^p - 1)\varrho_0 a_3^m / b_3^m, \\ \bar{\varkappa}_s^m &= \varrho_0 \varkappa_s^m / b_s^m, & \bar{\varkappa}_3^m &= -\phi_3(\varkappa_s^p - 1)\varrho_0 a_3^m / b_3^m, \\ \bar{c}_{vs} &= c_{vs} + T_r (b_s^T)^2 / b_s^m, & \bar{b}_s^T &= \varrho_0 T_r b_s^T / b_s^m, \\ \bar{c}_{v3} &= c_{v3} + T_r (b_3^T)^2 / b_3^m, & \bar{b}_3^T &= \varrho_0 T_r b_3^T / b_3^m, \\ \bar{a}_3^T &= a_3^T + a_3^m b_3^T / b_3^m, & \Gamma^m &= S_1^m \Gamma_3^m / (\Gamma_1^m + \Gamma_3^m), \\ \Lambda^T &= \Lambda_s^T \Lambda_3^T T_r / (\Lambda_s^T + \Lambda_3^T). \end{aligned}$$

The unknowns here are: $\mathbf{u}_s$, $\vartheta_s$, $\vartheta_3$, $\mu_1$, $\mu_3$. The number of equations (6.18) is adequate for their determination. Further simplification of these equations can be possible following experimental estimation of the constants existing in Eqs. (6.18) for any individual dried material and drying process.

The initial and boundary condition ought to be formulated in a similar way as in the theory of thermoelasticity but they must become completed by mass transfer conditions. For example, the heat and mass transfer boundary conditions for convective means of drying based on the present theory ought to be

$$\begin{aligned} \alpha_{sT}(\vartheta_a - \vartheta_s|_{\partial\mathscr{B}}) &= -\lambda_s \operatorname{grad}\vartheta_s|_{\partial\mathscr{B}} \cdot \mathbf{n}, \\ \alpha_{3T}(\vartheta_a - \vartheta_3|_{\partial\mathscr{B}}) &= -\lambda_3 \operatorname{grad}\vartheta_3|_{\partial\mathscr{B}} \cdot \mathbf{n} + c_{p3}\vartheta_3 \boldsymbol{\eta}_3|_{\partial\mathscr{B}} \cdot \mathbf{n}, \\ \alpha_{3m}(\mu_a - \mu_3|_{\partial\mathscr{B}}) &= -\gamma_3 \operatorname{grad}\mu_3|_{\partial\mathscr{B}} \cdot \mathbf{n} - \gamma_3^{*T} \operatorname{grad}\vartheta_3|_{\partial\mathscr{B}} \cdot \mathbf{n}. \end{aligned} \tag{6.19}$$

The terms on l.h.s. of Eqs. (6.19) describe the convective heat and mass transfer between the surrounding and the boundary surface. The terms on r.h.s. of Eqs. (6.19) are the heat and mass transport equations (5.8) and (5.10), respectively.

The end of the drying process is when $\vartheta_a = \vartheta_s|_{\partial\mathscr{B}} = \vartheta_3|_{\partial\mathscr{B}}$ and $\mu_a = \mu_3|_{\partial\mathscr{B}}$.

## 7. Plunge of the evaporation surface

In some cases of dried materials, e.g., for capillary-porous materials with relatively large pore dimensions, the evaporation surface may recede from the boundary towards the inside of the material. Thus the interior of the dried material is divided into two regions, wet and dry, separated by the evaporation surface being a singular surface for some functions. The problem of heat and mass transfer in such a case is mathematically formulated as that with moving boundaries, which may be referred to as an example of the Stefan problem (see [26]). We then need some extra conditions concerning the singular surface.

To determine these conditions we shall refer to the balance equations in an interface given, for example, by MOECKEL [35] or KOSIŃSKI [21]. For clarity, we shall say that the pore space is filled up with a fluid being a gas in a region denoted by "$-$" and a liquid in a region "$+$" (see Fig. 4). It is assumed here that the skeleton of the medium does not suffer any discontinuity.

For the fluid in the pore space, the equations of balance of mass, momentum and energy in the interface read (see [35], Eqs. (4.5) to (4.7)):

$$[|\varrho_f(v_{fN} - V_N)|] = 0, \tag{7.1}$$

$$[|\varrho_f \mathbf{v}_f(v_{fN}-V_N)|] = [|P_f|]\mathbf{N}+\mathrm{div}_s\mathbf{S}, \tag{7.2}$$

$$\left[\left|\varrho_f\left(u_f+\frac{1}{2}\mathbf{v}_f\cdot\mathbf{v}_f\right)(v_{fN}-V_N)\right|\right] = [|P_f v_{fN}-\mathring{q}_{fN}|]+\mathrm{tr}\{(\mathrm{grad}_s\mathbf{U})\mathbf{S}^T\}-\mathrm{div}_s\mathbf{q}^s, \tag{7.3}$$

where $\varrho_f$, $\mathbf{v}_f$, $P_f$, $u_f$ and $\mathring{\mathbf{q}}_f$ are the partial mass density, the velocity, the partial pressure, the internal energy, and the heat flux vector of the fluid, respectively, $\mathbf{V}$ is the velocity of receding of the evaporation surface, $\mathbf{S}$ is the surface stress, $\mathbf{q}^s$ is the surface heat flux vector and $\mathbf{U}$ is the particle velocity in the surface. The index $N$ denotes "normal to the evaporation surface", e.g., $v_{fN} = \mathbf{v}_f\cdot\mathbf{N}$. The difference $\psi^+-\psi^- = [|\psi|]$ is called the jump of $\psi$ on the surface $\Sigma_0$.

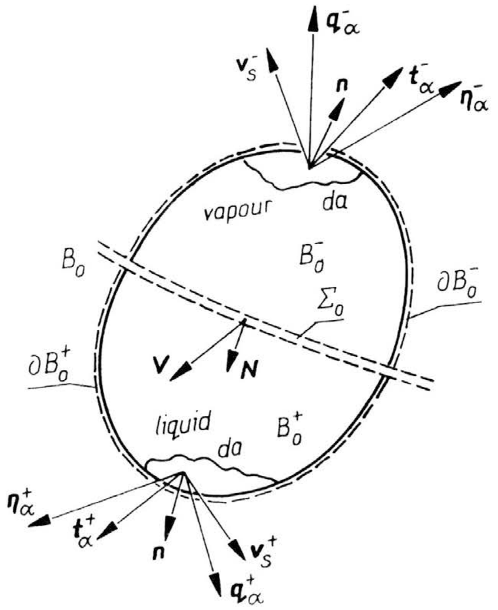

FIG. 4. Plunge of the evaporation surface.

As the phase transition surface is not to be material, other terms related to the surface mass do not exist in Eqs. (7.1) to (7.3).

Equation (7.1) can be regarded as the one which determines the velocity of receding of the evaporation surface. This is easily seen when rearranging Eq. (7.1) as follows:

$$V_N-v_{0N} = \frac{[|\eta_{fN}|]}{[|\varrho_f|]} = \frac{\eta_{lN}-\eta_{gN}}{\varrho_l-\varrho_g}, \tag{7.4}$$

where $\eta_{fN} = \varrho_f(v_{fN}-v_{0N})$ is the mass flux vector of the fluid, and the subscripts $l$ and $g$ denote liquid and gas, respectively. We see from Eq. (7.4) that if the influx of the liquid to the evaporation surface is equal to the efflux of gas from it, then the relative motion of the evaporation surface with respect to the matrix ($V_N-v_{0N}$) is equal to zero. Otherwise the surface moves and $\eta_{lN} > \eta_{gN}$ means condensation, and $\eta_{lN} < \eta_{gN}$ means evaporation.

Practically, it can be assumed that

$$v_{0N} \cong 0, \quad \eta_{lN} \cong 0, \quad \varrho_l \gg \varrho_g, \tag{7.5}$$

and thus

$$V_N \cong -\eta_{gN}/\varrho_l. \tag{7.6}$$

The minus sign means that $V_N$ has the opposite direction to $\eta_{gN}$.

Let us multiply Eq. (7.2) by **N**. Referring to Slattery (see [41], p. 56), we identify

$$\mathrm{div}_s \mathbf{S} \cdot \mathbf{N} = -2H\sigma\Phi, \tag{7.7}$$

where $\sigma$ is the surface tension, $H$ is the mean curvature of the meniscus in capillary-pores, and $\Phi$ is the porosity ratio. Rearranging Eq. (7.2) and using Eqs. (7.5) and (7.6), we can write

$$P_l = P_g + 2H\sigma\phi - \varrho_g V_{gN}^2. \tag{7.8}$$

If the kinetic energy of gas (dynamic pressure of gas) can be neglected (no thermal shocks as in casting moulds), then we obtain the familiar Laplace formula (see, e.g., [43], p. 188).

We can consider Eqs. (7.6) and (7.8) as the boundary conditions for mass and momentum transfer on the interface. The condition for heat transfer on the interface is to be obtained from Eq. (7.3). We assume, however, that the energy-sharing of the evaporation surface in the total amount of energy is negligibly small (see [43], p. 180). Therefore we omit in Eq. (7.3) the terms $\mathrm{tr}\{(\mathrm{grad}_s \mathbf{U})\mathbf{S}^T\}$ and $\mathrm{div}_s \mathbf{q}^s$ as well as the kinetic energy $\frac{1}{2}\mathbf{v}_f \cdot \mathbf{v}_f$.

Using Eq. (4.9), we can rearrange Eq. (7.2) as follows:

$$[|\mu_f|] < \varrho_f(v_{fN} - V_N) > = [|P_f V_N - q_{fN} + \varrho_f s_f T_f (V_N - v_{0N})|], \tag{7.9}$$

where $\mu_f$ is the fluid potential defined similarly as in Eq. (4.14) and $\langle\psi\rangle = \frac{1}{2}(\psi^+ + \psi^-)$ means an average quantity of $\psi$ on the interface. As we have already mentioned, (see Eq. (5.26)), the fluid potential consists of the chemical potential and capillary potential. The former is continuous on the interphase surface i.e., $[|\mu_f^{\mathrm{ch}}|] = 0$ (see [12] p. 182). The jump of the capillary potential reads

$$[|\mu_f^{\mathrm{cap}}|] = \overset{+}{\mu}{}_f^{\mathrm{cap}} - \overset{-}{\mu}{}_f^{\mathrm{cap}} \cong \overset{+}{\mu}{}_f^{\mathrm{cap}} = -2H\sigma/\varrho_l^t, \tag{7.10}$$

where $\varrho_l^t$ is the true mass density of the liquid. Using Eqs. (7.5) and (7.6), we state that $\langle\varrho_f(v_{fN} - V_N)\rangle = -\varrho_l V_N$. On the basis of Eq. (7.8), neglecting the dynamic pressure, we know that $[|P_f|] = 2H\sigma\Phi$.

Thus the term on l.h.s. of Eq. (7.9) reduces with the first term on r.h.s. of Eq. (7.9), and we finally obtain

$$[|q_{fN}|] = -\varrho_l l V_N, \tag{7.11}$$

where

$$\varrho_l l \overset{\mathrm{df}}{=} (\varrho_f^- s_f^- - \varrho_f^+ s_f^+) T_f, \tag{7.12}$$

is the latent heat of evaporation (see [12], p. 183), and

$$T_f \equiv T_f^+ = T_f^- \tag{7.13}$$

is the phase transition temperature being constant on the interphase surface. The heat flux vector is determined similarly as in Eq. (5.8), i.e.,

$$q_{fN} = -\lambda_f \operatorname{grad}_N T_f + c_{pf}\vartheta_f \eta_{fN}. \tag{7.14}$$

Equation (7.11) describes the heat balance across the interface. As to deformations of dried materials with receding evaporation surface, we determine them using the field equations presented in the preceding sections. However, we can assume that the amount of bound liquid is negligibly small in comparison to the amount of free liquid and that there is no liquid in the "−" region. If the phase transition is neglected inside the "−" region, then the set of field equations (6.1) to (6.8) can be utilized. We must only differentiate them for "+" and "−" regions. For example, the physical relations (6.2) are

$$\overset{+}{\mathbf{T}}_s = 2\overset{+}{M}\overset{+}{\mathbf{E}}_s + (\overset{+}{A}\operatorname{tr}\overset{+}{\mathbf{E}}_s - \overset{+}{\varkappa}{}_s^T\overset{+}{\vartheta} - \overset{+}{\varkappa}{}_s^m\overset{+}{\theta})\mathbf{I} \tag{7.15$_1$}$$

for the "+" region, and

$$\overset{-}{\mathbf{T}}_s = 2\overset{-}{M}\overset{-}{\mathbf{E}}_s + (\overset{-}{\mathbf{A}}\operatorname{tr}\overset{-}{\mathbf{E}}_s - \overset{-}{\varkappa}{}_s^T\overset{-}{\vartheta} - \overset{-}{\varkappa}{}_s^m\overset{-}{\theta})\mathbf{I} \tag{7.15$_2$}$$

for the "−" region. Here $\overset{+}{\theta} = \varrho_l/\varrho_0$ and $\overset{-}{\theta} = \varrho_g/\varrho_0$. All quantities related to the solid matrix are assumed to be continuous on the interface. The discontinuity of quantities related to the fluid filling the pore space is given by the conditions developed in this section. Thus the solution of the problem of drying with moving evaporation surface is possible.

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