

# APPLICATION OF IRREVERSIBLE THERMODYNAMICS METHODS TO INVESTIGATION OF HEAT AND MASS TRANSFER\*

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**Аннотация**—На основе феноменологической теории—термодинамики необратимых процессов, а также исходя из отдельных результатов кинетической и статистической теорий, приводится систематическое описание явлений переноса—теплопроводности с учетом конечной скорости распространения тепла, релаксации напряжений в вязко-упругих телах, переноса влаги в капиллярно-пористых телах, а также процессов турбулентного переноса. Приведены некоторые решения гиперболического уравнения массопереноса в пористых телах.

## NOMENCLATURE

$a$ ,	thermal diffusivity ( $a = \lambda/c\rho$ );	$S$ ,	entropy;
$b$ ,	degree of filling capillaries of a body with liquid;	$T$ ,	temperature;
$c$ ,	specific heat;	$v_m$ ,	molecular velocity;
$C$ ,	concentration;	$u$ ,	internal energy or relative moisture concentration in a porous body (moisture content);
$D_{\text{cap}}$ ,	capillary diffusivity;	$w$ ,	fluid flow velocity or propagation velocity of stresses, heat or mass;
$D_m$ ,	moisture diffusivity in a body, or mass diffusivity in a gaseous mixture flow;	$X_i$ ,	thermodynamic driving forces.
$D_T$ ,	turbulent diffusivity;	Greek symbols	
$E$ ,	phase transformation number;	$\epsilon$ ,	shear strain;
$G$ ,	shear modulus;	$\dot{\epsilon} = d\epsilon/d\tau$ ,	shear strain rate;
$J$ ,	specific heat or mass flux;	$\eta$ ,	viscosity;
$k$ ,	capillary conductivity;	$\theta$ ,	contact angle;
$n$ ,	direction of the normal to isothermal surface;	$\lambda$ ,	thermal conductivity;
$n_i$ ,	concentration of the $i$ -th component;	$\mu_i$ ,	chemical potential of the $i$ -th component;
$p$ ,	pressure or shear stress;	$\Pi$ ,	void fraction of a body;
$\dot{p} = dp/d\tau$ ,	rate of time change of shear stress;	$\rho$ ,	density;
$q$ ,	specific heat flux;	$\rho_0$ ,	density of an absolutely dry body;
$\dot{q} = dq/d\tau$ ,	rate of time change of specific heat flux;	$\sigma$ ,	entropy production or surface tension coefficient;
$L$ ,	specific heat of phase transformation;	$\tau$ ,	time;
		$\psi$ ,	capillary potential of a body.

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## Dimensionless numbers

$Lu$ , ratio of the moisture-content field

to the temperature field in a porous body

$$(Lu = D_m/\alpha = D_{mc}\rho_0/\lambda);$$

$Pn$ , the Posnov number

$$(Pn = \delta(u_a - u_0)/(T_a - T_0)).$$

Subscripts

$q$ ,	thermal state;
$c$ ,	elastic state;
$m$ ,	characteristic of the mass of material or molecular characteristics;
$T$ ,	turbulent properties;
$t$ ,	isothermal state;
$r$ ,	relaxation characteristics.

### 1. PRINCIPLES OF THE THEORY

THE THEORY of transfer processes covers such diverse phenomena as diffusion, heat conduction, thermal diffusion, electrical conduction, absorption of sound waves, etc.

Transfer phenomena occur in the system which, strictly speaking, is not in a state of thermodynamic equilibrium. Two types of transfer phenomena should be distinguished:

Firstly processes taking place in the system, whose initial state is not that of equilibrium but which when left to itself passes to an equilibrium state. All relaxation phenomena are such processes.

Secondly, processes taking place in the system where external effects (for example, temperature gradients maintained from the outside, variable external fields) prevent the equilibrium state from setting in. In the system which is affected by external effects, generally speaking a steady state sets in, which should be distinguished from that of equilibrium.

The aim of the transfer theory is to investigate both these types of transfer process.

There are three main methods of treating transfer processes.

First, the kinematic theory which presents the most direct method of treatment of irreversible processes. Here from the very beginning, a certain particular model of the system is assumed. Probabilities of molecular collisions obtained with this model serve for the derivation of certain kinetic equations, for example, the Boltzmann equation.

The second, rather general, method is the statistical mechanics of irreversible processes. Its aim is the development of a general formalism similar to the algorithm of the statistic sum in the statistical mechanics of equilibrium states. This formalism should make it possible to predict according to a certain procedure any macroscopic property of the system in which an irreversible process takes place. In this case no special model is adopted. With this approach, however, certain fundamental difficulties are encountered [1].

The last method, which is adopted in the present work, is used for studying transfer processes with the aid of the phenomenological theory of thermodynamics of irreversible processes, but requires the two other methods for its justification.

The thermodynamics of irreversible processes is a powerful phenomenological method for the investigation of heat and mass transfer. It is widely adopted in macroscopic research on heat, mass and energy transfer. As was shown by de Groot [2], the equations of hydrodynamics of continuous media are obtained directly from the basic equations of non-equilibrium thermodynamics. Using these methods one can obtain equations of energy, heat and mass transfer for various systems including non-Newtonian fluids and disperse media, and derive some features of the turbulent heat- and mass-transfer theory. All these problems will be discussed in this paper.

The basis of irreversible thermodynamics is a known equation relating the rate of entropy production to the fluxes  $d_i S$  (for example, heat or diffusion fluxes, etc.) and the thermodynamic forces  $X_i$  giving rise to these fluxes (temperature gradient, concentration gradient, etc.):

$$\sigma = \frac{d_i S}{d\tau} = \sum_i J_i X_i \geq 0. \quad (1.1)$$

Equation (1.1) may be derived from the Gibbs equation:

$$TdS = du + p dV - \sum_i \mu_i dn_i \quad (1.2)$$

Relations (1.1) and (1.2) assume that the entropy of the system, which is not in the equilibrium state, is determined by the same independent variables as in the equilibrium state.

The postulate (1.2) which shows the possibility of describing non-equilibrium states by variables which are strictly speaking defined for equilibrium systems only, is not obvious. However, as Prigogine has shown using kinetic theory, it is a rather good approximation when the deviations from the equilibrium state are not too large.

For the transfer processes, the irreversible thermodynamics based on relation (1.1) is restricted to the domain of validity of the linear phenomenological laws

$$J_i = \sum_k L_{ik} X_k \quad (1.3)$$

where the phenomenological coefficients  $L_{ik}$  are assumed *constant*. This is important and should be remembered when taking into account in the essentially linear equations (1.3) the empirical dependence of the phenomenological coefficients  $L_{ik}$  on the variables which enter into the definition of the thermodynamic forces. Strictly speaking, this is not correct within the framework of the thermodynamics of irreversible processes.

Besides, there are reciprocal relations which follow from the microscopic reversibility:

$$L_{ik} = L_{ki}. \quad (1.4)$$

Conditions (1.3) and (1.4) are more severe than the conditions of validity of the Gibbs equation. From relations (1.1), (1.3) and (1.4) it follows that these coefficients determine the completely defined square form  $\sum_{i,k} L_{ik} X_i X_k \geq 0$  for all  $X_i$  and in particular,  $L_{ii} L_{kk} \geq L_{ik}^2$ .

Also, equations (1.3) should be co-variant, i.e. all their terms should be of the same tensor dimension.

Relations (1.1–1.4) are usually applied to the steady-state transfer processes, but as de Groot has shown, they may also be used for low-rate steady-state phenomena.

In high-rate unsteady-state transfer processes, the phenomenological coefficients entering relation (1.3) cannot be considered as constant. Therefore the basic requirement of linearity of the phenomenological transfer laws is not satisfied. The linear transfer equations change in this case into non-linear equations and relations (1.1) and (1.3) must be examined more closely.

Following Prigogine [3], we divide the total change of entropy production rate  $d\sigma$  for the time  $d\tau$  into two parts: one,  $d_x\sigma$ , referring to the change of thermodynamic forces, the other,  $d_J\sigma$ , referring to the change of flux:

$$d\sigma = d_x\sigma + d_J\sigma = \sum_i J_i dX_i + \sum_i X_i dJ_i \quad (1.5)$$

Prigogine has proved that when phenomenological coefficients are constant and reciprocal relations are valid, the contribution to the rate of entropy production due to the change of thermodynamic forces is equal to that due to the change of fluxes  $J_i$ .

Thus,

$$d_x\sigma = d_J\sigma = \frac{1}{2} d\sigma \quad (1.6)$$

$$\sum_i J_i \frac{dX_i}{d\tau} = \sum_i X_i \frac{dJ_i}{d\tau} \quad (1.7)$$

In the whole region of validity of irreversible thermodynamics, the relation

$$d_x\sigma \leq 0 \quad (1.8)$$

holds.

In transient high-rate processes the fluxes  $J_i$  are related to their thermodynamic forces  $X_k$  by certain non-linear equations, the form of which is, generally speaking, unknown. If, however, the deviation from the equilibrium state is not very large, these non-linear laws may be approximately expressed in the following way:

$$J_i = L_i^{(r)} \dot{J}_i + \sum_k (L_{ik} X_k + L'_{ik} \dot{X}_k) \quad (1.9)$$

where  $L_i^{(r)}$ ,  $L_{ik}$  and  $L'_{ik}$  are constant phenomenological transfer coefficients. In steady-state transfer processes  $\dot{X}_i = \dot{J}_i \equiv 0$  and an ordinary linear equation is obtained from equation (1.9)

$$J_i = \sum_k L_{ik} X_k.$$

If the rate of change of the thermodynamic forces is small, equation (1.9) may be written as follows

$$J_i = L_i^{(r)} \dot{J}_i + \sum_k L_{ik} X_k \quad (1.10)$$

where  $L_i^{(r)}$  is measured in time units and may be called a relaxation coefficient. Such a situation occurs, for example, in heat-conduction processes in those cases when the time  $L_i^{(r)}$  is comparable with the time of the unsteady-state heat-conduction process (see Section 3).

Sometimes, for example, in describing moisture transfer in a capillary-porous body, the terms containing the time derivatives of the thermodynamic forces should also be taken into account.

## 2. RELAXATION OF STRESSES IN VISCO-ELASTIC BODIES

As the first illustration and to explain the physical significance of the additional terms entering equation (1.10), we shall consider the momentum transfer of regular motion in visco-elastic (non-Newtonian) fluids.

A hundred years ago Maxwell assumed the absence of any essential differences in the mechanical properties of viscous fluids and solids on the basis of the relaxation concept. Relaxation is a progressive resolution of elastic stresses with a constant prescribed strain, i.e. a progressive dissipation by transformation into heat of the elastic energy in a body under strain. Relaxation processes are inseparably connected with random thermal molecular motion. Shear stresses  $p_{ik}$  in a visco-elastic body relax over a time interval  $\tau_r$  at a certain finite rate  $w_r$ .

We shall assume that the relaxation of the internal stresses  $p_{ik}$  follows the Maxwellian law

$$p_{ik} = p_{ik}(0) \exp\left(-\frac{\tau}{\tau_r}\right) \quad (2.1)$$

where  $\tau_r$  is the relaxation time which equals the ratio of the viscosity  $\eta$  to the shear modulus  $G$  ( $\tau_r = \eta/G$ ). Thus in a visco-elastic body, shear stresses relax at a rate which is inversely proportional to the viscosity:

$$\dot{p}_{ik} = -\frac{1}{\tau_r} p_{ik} = -\frac{G}{\eta} p_{ik}. \quad (2.2)$$

In an elastic body the shear stresses remain constant ( $p_{ik} = p_{ik}(0)$ ), or the relaxation time  $\tau_r \rightarrow \infty$ . Thus, if  $\tau_r \rightarrow \infty$ , then the liquid behaves like an amorphous solid.

Newtonian fluids may be considered as visco-elastic bodies with relaxation time  $\tau_r \rightarrow 0$ , or with the relaxation rate  $w_r \rightarrow \infty$ . Thus, if  $\tau_r \rightarrow 0$ , a body behaves as an ordinary viscous fluid. For such fluids, shear stress is directly proportional to the viscosity and to the rate of shear strain  $\dot{\epsilon}_{ik}$  (the law of viscous flow). Indeed,

for an incompressible parallel plane flow the shear stress may be written as follows:

$$\begin{aligned} p_{12} &= -\eta \left( \frac{\partial w_1}{\partial x_2} + \frac{\partial w_2}{\partial x_1} \right) \approx -\eta \frac{\partial w_1}{\partial x_2} \\ &= \eta \frac{\partial}{\partial \tau} \left( -\frac{\partial l_1}{\partial x_2} \right) \quad (2.3) \\ &= \dot{\epsilon} \eta_{12} \end{aligned}$$

In this case it is assumed that

$$\frac{\partial w_1}{\partial x_2} \gg \frac{\partial w_2}{\partial x_1}$$

In high-rate transient flows a viscous fluid behaves as a visco-elastic body. Newton's law (2.3) of viscous flow is therefore not valid and instead the relation (1.10) should be used. This may be written as follows:

$$p_{ik} = \eta \dot{\epsilon}_{ik} - \tau_r \dot{p}_{ik} = \eta \dot{\epsilon}_{ik} - \frac{\eta}{G} \dot{p}_{ik} \quad (2.4)$$

assuming the flux to be equal to  $p_{ik}$ ,  $\dot{\epsilon}_{ik}$  to the thermodynamic force,  $L_{11} = \eta$ , i.e. to the viscosity, and  $L_1^{(r)} = -\tau_r$  i.e. to the relaxation time.

If the relaxation time is short

$$\left( \tau_r = \frac{\eta}{G} \rightarrow 0 \right),$$

then from equation (2.4) the law of a viscous flow is obtained. If the viscosity  $\eta$  is large ( $\eta \rightarrow \infty$ ), then from equation (2.4) Guck's equation of elasticity is obtained

$$\dot{\epsilon}_{ik} = -\frac{1}{G} \dot{p}_{ik} \quad (2.5)$$

whence

$$p_{ik} = G \epsilon_{ik} = \rho w_c^2 \dot{\epsilon}_{ik} \quad (2.6)$$

Here  $w_c$  is the velocity of propagation of shear strain or the velocity of cross-wave propagation

$$w_c = \sqrt{(G/\rho)} \quad (2.7)$$

where  $\rho$  is the density.

In high-rate unsteady-state flows the value of  $\tau_r \dot{p}_{ik}$  is comparable with that of  $\eta \dot{\epsilon}_{ik}$ , so that equation (2.4) rather than (2.3) should be used.

For more complex structural systems the flow law is described by a more complex equation (1.9). For example, Oldroyd [4] has theoretically obtained a flow equation for a visco-elastic system consisting of emulsions and suspensions of one Newtonian fluid in another in the following form

$$p_{ik} = \eta \dot{\epsilon}_{ik} + \eta' \dot{\epsilon}'_{ik} - \tau_r \dot{p}_{ik} \quad (2.8)$$

Oldroyd's equation is identical with equation (1.9) at  $L = \eta$ ,  $L' = \eta'$ ,  $L^{(\tau)} = -\tau_r$ .

Returning to equation (1.10), it should be emphasized that the additional term  $L_i^{(\tau)} \dot{J}_i$  characterizes the finite velocity of propagation of stresses in a body or a body system.

### 3. HEAT TRANSFER

Similarly, in high-rate unsteady-state transfer processes instead of the linear heat-conduction Fourier law

$$J_q = L_{qq} X_q = -\lambda \nabla T, \quad (3.1)$$

one should use relation (1.10) viz.:

$$J_q = L_q^{(\tau)} \dot{J}_q + L_{qq} X_q \quad (3.2)$$

which we may write in the form

$$\vec{q} = -\lambda \vec{\nabla} T - \tau_r \dot{\vec{q}} \quad (3.3)$$

where  $\lambda$  is the heat-conduction coefficient, and  $L_q^{(\tau)} = -\tau_r$  is the relaxation time of the thermal stress.

Relation (3.3) has been obtained in [7-8] for the case of heat transfer and diffusion. The finite velocity of heat propagation  $w_q$  is

$$w_q = \sqrt{a/\tau_r} = \sqrt{(\lambda/c\rho\tau_r)} \quad (3.4)$$

where  $a = (\lambda/c\rho)$  is the thermal diffusivity. For nitrogen  $w_q = 150$  m/sec, and  $\tau_r = 10^{-9}$  s while for metals  $\tau_r$  is even smaller, for example, for aluminium  $\tau_r = 10^{-11}$  s. Therefore in these cases experimental measurement of  $\tau_r$  is impossible. For gases, however, under the conditions of rarefied supersonic flow, the effect of a finite velocity of heat propagation on heat transfer becomes pronounced.

Equation (3.3) may be written as follows

$$\vec{q} = -\lambda \vec{\nabla} T - \frac{\lambda}{c\rho w_q^2} \dot{\vec{q}} \quad (3.5)$$

In the classical heat-conduction theory it is assumed that heat propagation velocity  $w_q$  is infinitely large ( $w_q \rightarrow \infty$ ). Assuming  $w_q \rightarrow \infty$ , from equation (3.5) we obtain the Fourier heat-conduction law which corresponds to the case when the relaxation time of heat stress is assumed to be zero ( $\tau_r = 0$ ).

With high rates of change of the heat-flux  $\dot{q}$ , the second term in equation (3.5) becomes comparable with the first one and cannot be neglected.

If the heat-conduction coefficient is large ( $\lambda \rightarrow \infty$ ), or volumetric heat capacity is small ( $c\rho \rightarrow 0$ ), then from equation (3.5) we obtain

$$q \sim c\rho w_q^2 \frac{T}{w_t}$$

where  $w_t$  is the propagation velocity of the isotherm, proportional to thermal diffusivity. The form of equation (3.6) is similar to that of equation (2.6) which describes stress propagation in a body with a very long relaxation time ( $\tau_r \rightarrow \infty$ ).

On the basis of equation (3.5), we may obtain the differential heat-transfer equation. Indeed, eliminating the flux  $q$  from the heat-balance equation for a one-dimensional problem

$$c\rho \frac{\partial T}{\partial \tau} = -\frac{\partial q}{\partial x} \quad (3.7)$$

and from equation (3.5), we obtain

$$\frac{\partial T}{\partial \tau} + \tau_r \frac{\partial^2 T}{\partial \tau^2} = a \frac{\partial^2 T}{\partial x^2} \quad (3.8)$$

Equation (3.7) is of hyperbolic type and allows for the effect of heat propagation velocity.

With low gas pressures when the value of volumetric heat capacity is small ( $c\rho \rightarrow 0$ ), heat is transferred by the molecular mechanism. In this case the length of the mean molecular free path determines the value of the thermal conductivity and the heat propagation velocity. Then the first term may be neglected and we shall finally obtain the heat-transfer equation in the form

$$\frac{\partial^2 T}{\partial \tau^2} = w_a^2 \frac{\partial^2 T}{\partial x^2} \quad (3.9)$$

This relation holds for gases under the conditions of supersonic flow with small rarefactions.

In Appendix I it is shown that the heat-transfer equations are of hyperbolic type if they are to account for a finite heat-propagation velocity. This result follows from the kinetic theory by the solution of the Boltzmann equation by Grad's method [9].

Finally, it is of interest to show the analogy between the results presented here and the known case of calculation of the finite heat-propagation velocity (the Zeldovich-Kompaneets temperature waves [10]), where it is derived from a power function dependence on the thermal properties of the medium on temperature.

#### 4. MASS TRANSFER IN COLLOIDAL CAPILLARY-POROUS BODIES

Moist materials are hydrophilic capillary-porous bodies. In such bodies osmotic bound moisture and adsorption bound moisture are transferred by molecular mechanism according to Fick's diffusion law. As in the case of molecular heat transfer, it is assumed that the mass velocity is infinite. This assumption in the analytical diffusion theory does not affect the final results, since the relaxation time in molecular mass transfer is approximately of the same order as the relaxation time for heat transfer.

However simultaneously with moisture diffusion in colloidal capillary-porous bodies a slow motion of the moisture occurs due to capillary forces. Usually the capillary motion of moisture in a polycapillary-porous body is well described by the moisture-transfer law, which is analogous to the diffusion law (capillary diffusion). The capillary potential is assumed to be a continuous function of the moisture content of the body, so that the gradient of the capillary potential is proportional to the gradient of the moisture content. Thus the capillary-moisture flow  $j_{\text{cap}}$  will be

$$\vec{j}_{\text{cap}} = k \nabla \psi \quad (4.1)$$

where  $k$  is the capillary conductance which is equal to

$$k = \frac{\rho^2}{8\eta} \int_{r_0}^r r^2 f(r) dr \quad (4.2)$$

$f(r)$  is the differential curve of the distribution of the pore sizes by their radius  $r$  which varies in a body from a certain minimum value  $r_0$  to a maximum one  $r$  at the given moisture content  $u$  (the maximum radius of capillaries filled with liquid).

Under isothermal conditions the gradient of the capillary potential  $\nabla \psi$  is proportional to the gradient of the moisture content  $\nabla u$ , so that we may write

$$\vec{j}_{\text{cap}} = -D_{\text{cap}} \rho_0 \nabla u \quad (4.3)$$

where  $D_{\text{cap}}$  is the capillary diffusivity equal to

$$D_{\text{cap}} = \frac{\sigma \cos \theta}{4\eta r^2 f(r)} \int_{r_0}^r r^2 f(r) dr \quad (4.4)$$

where  $\sigma$  is the surface-tension coefficient, and  $\theta$  the contact angle between the capillary walls and the liquid.

Formula (4.3) is valid for a porous body of the polycapillary structure. For a moncapillary body  $f(r) \rightarrow \infty$ , and therefore  $k \rightarrow \infty$ , and  $\nabla \psi \rightarrow 0$ . In this case the flow of capillary-moisture will be

$$\vec{j}_{\text{cap}} = \Pi \rho b w_{\text{cap}} \quad (4.5)$$

where  $\Pi$  is the void fraction of a body,  $b$  the degree of filling of the capillaries with liquid,  $w_{\text{cap}}$  the mean liquid velocity in a body of the moncapillary structure.

Formula (4.3) is similar to Fick's equation for osmotic-moisture diffusion. It is assumed that the velocity of propagation of moisture is infinitely large as in the case of heat propagation. In reality in colloidal capillary-porous bodies, the moisture (liquid) velocity is of the order of  $2 \times 10^{-2}$  m/s to  $5 \times 10^{-2}$  m/s, while the moisture diffusion coefficient  $D_m$  for various bodies ranges from  $1.4 \times 10^{-8}$  m/s to  $30 \times 10^{-8}$  m/s [11]. Thus the relaxation time  $\tau_{rm}$  will be of the order of  $0.4-1.2 \times 10^{-4}$  s, i.e. it is as much as

$10^5$ – $10^7$  times larger than that for heat transfer in gases and metals.

Consequently, the moisture transfer in a colloidal capillary-porous body of the poly-capillary structure must be described by means of the generalized moisture transfer law (1.10), i.e.

$$\vec{j} = -D_m \rho_0 \nabla u - \tau_m \frac{\partial \vec{j}}{\partial \tau} \quad (4.6)$$

where  $D_m$  is moisture-diffusion coefficient,  $\tau_m$  the time of moisture propagation in a capillary-porous system, which equals

$$\tau_{rm} = D_m / w_{rm}^2.$$

If the capillary walls are slightly hydrophilic, then the capillary diffusivity of moisture may be assumed very large. From formula (4.6) we obtain

$$-\rho_0 \frac{\partial u}{\partial n} - \frac{1}{w_{rm}^2} \frac{\partial j}{\partial \tau} = \frac{j}{D_m} \rightarrow 0. \quad (4.7)$$

Denoting the linear velocity of the isoconcentration surface (the surface inside a body with equal relative concentration  $u$ ) by  $w_u = dn/d\tau$ , we obtain from (4.7)

$$j = \rho_0 \frac{w_{rm}^2}{w_u} \Delta u \quad (4.8)$$

where  $\Delta u$  is a certain fixed difference of moisture contents.

For a porous body of monocapillary structure we may approximately assume  $w_{rm} = w_u$ , and  $\Delta u$  is equal to the maximum moisture content  $u_\infty$  ( $\Delta u = u_\infty$ ), so that from formula (4.8) we obtain

$$j = \rho_0 w_{rm} u_\infty \quad (4.9)$$

i.e. relation (4.7), since in this case  $\rho_0 u_\infty = \Pi \rho b$ .

Thus for porous body of a monocapillary structure the mass-transfer rate  $w_{rm}$  is approximately equal to the rate of capillary-propagation ( $w_{rm} = w_{cap}$ ).

Besides, it follows from the above analysis that formula (4.6) describes moisture diffusion when the moisture propagation velocity due to capillary penetration is finite.

On the basis of moisture-mass conservation law for a one-dimensional problem, we have

$$\rho_0 \frac{\partial u}{\partial \tau} = -\frac{\partial j}{\partial x} \quad (4.10)$$

If we substitute from (4.6) for  $j$  and assume  $\tau_{rm} = D_m / w_{rm}^2$  constant, we obtain the differential equation of mass transfer in a colloidal capillary-porous body†

$$\frac{\partial u}{\partial \tau} + \tau_{rm} \frac{\partial^2 u}{\partial \tau^2} = D_m \frac{\partial^2 u}{\partial x^2} \quad (4.11)$$

This equation differs from the ordinary moisture-transfer equation by the additional term

$$\tau_{rm} \frac{\partial^2 u}{\partial \tau^2},$$

which characterizes capillary motion of moisture.

In the case of non-isothermal conditions the differential equation of moisture transfer in colloidal capillary-porous bodies is of the form

$$\frac{\partial u}{\partial \tau} + \tau_{rm} \frac{\partial^2 u}{\partial \tau^2} = D_m \left( \frac{\partial^2 u}{\partial x^2} + \delta \frac{\partial^2 t}{\partial x^2} \right) \quad (4.12)$$

where  $\delta$  is the thermogradient coefficient equal to the ratio of the coefficients of thermal diffusion in moisture and of moisture diffusion.

This equation should be solved simultaneously with the heat-conduction equation for a moist body

$$\frac{\partial T}{\partial \tau} = a \frac{\partial^2 T}{\partial x^2} + E \frac{L}{c} \frac{\partial u}{\partial \tau} \quad (4.13)$$

where  $L$  is the specific heat of phase conversion and  $E$  is the phase conversion number.

The set of differential equations (4.12)–(4.13) has been solved by Luikov and Perelman for the boundary conditions

$$T(x, 0) = T_0, \quad T(0, \tau) = T_a \quad (4.14)$$

$$\frac{\partial T(\tau, \infty)}{\partial x} = 0, \quad u(x, 0) = u_0 \quad (4.15)$$

$$\frac{\partial u(0, \tau)}{\partial \tau} = 0, \quad u(0, \tau) = u_a \quad (4.16)$$

$$\frac{\partial u(\tau, \infty)}{\partial x} = 0 \quad (4.17)$$

† The case when the capillary mass-transfer rate  $w_{rm}$  varies with position is discussed in Appendix II.

The analysis of the solution obtained shows that thermal diffusion of moisture has a considerable influence on the capillary moisture transfer at the finite rate  $w_{rm}$ . As an illustration we shall present the solution of the above problem (4.12–4.17) for a particular case of isothermal moisture transfer ( $\delta = 0$ ) with no phase changes ( $E = 0$ ). In this case the solution may be written as follows

$$u^* = \frac{u - u_0}{u_a - u_0} = H(\tau^* - \xi) \left\{ 1 - \frac{1}{\pi} \int_0^1 e^{-\tau^* z} \sin(\sqrt{z(1-z)}\xi) \frac{dz}{z} \right\} \quad (4.18)$$

where  $\tau^* = \tau/\tau_{rm}$  is the dimensionless time,  $\xi$  is a quantity equal to

$$\xi = \frac{x}{\sqrt{[D_m \tau_{rm}]}} \quad (4.19)$$

while  $H(\tau^*)$  is equal to

$$H(\tau^*) = \begin{cases} 0 & \text{at } \tau^* < 0 \\ 1 & \text{at } \tau^* > 0 \end{cases} \quad (4.20)$$

Formula (4.18) describes moisture transfer at a finite rate (at  $\tau^* > \xi$ ). Moisture reaches the point  $x$  at a time  $\tau \geq \frac{\sqrt{(\tau_{rm})}}{D_m} x$ . At points farther removed from the surface moisture is still absent [ $H(\tau^* - \xi) = 0$ ].

The solution of the problem with infinitely large moisture-transfer rate ( $\tau_{rm} = 0$ ) is known to be of the form

$$u^* = \operatorname{erfc} \left( \frac{x}{2\sqrt{[D_m \tau]}} \right) \quad (4.21)$$

Solution (4.21) differs from solution (4.18). They coincide only at  $\tau \rightarrow \infty$ . For  $\tau^* \rightarrow \infty$  we obtain from solution (4.18)

$$u^* = 1 - \frac{\eta}{\sqrt{\pi \tau^*}} + \dots = 1 - \frac{x}{\sqrt{\pi D_m \tau}} + \dots \quad (4.22)$$

which is identical with (4.21) at  $\tau \rightarrow \infty$ .

Thus, the generalized relations of thermodynamics of irreversible transient transfer processes can describe the capillary-diffusion transfer in moist materials.

To conclude this section it should be noted

that, as estimations have shown in a number of cases of moisture transfer in a complex and tangled system of capillaries, to which type belong a capillary-porous body, the terms containing the time derivatives of the thermodynamic forces should also be included [see equation (1.9)].

## 5. TURBULENT HEAT- AND MASS-TRANSFER PROCESSES

Transport phenomena, e.g. of heat, momentum and mass, are of fundamental importance in turbulent flow. Because of the special treatment of the subject in this paper and the shortage of space, only a very brief summary will be given now of the information obtained concerning the theory of turbulent transfer including the finite velocities of propagation. New methods of description of the processes of turbulent transfer will be published elsewhere.

Typical of the transfer processes in turbulent flows is the great variety of scales of the turbulent motions that stir the medium. The character of the turbulent transfer is determined by the energy distribution between the turbulent motions of different scales. The largest of the motion scales which contains almost the whole energy of the stream is called the scale of turbulence,  $l$ . The values of fluid velocity at points distance from each other by no more than  $l$ , are statistically interconnected. Therefore the particles of liquid or admixture, the distance between which does not exceed  $l$ , will not move independently of each other. This breaks the analogy between turbulent and molecular transfer.

As a rule, however, the region in which transfer occurs is considerably larger than the scale of turbulence. In such cases the description of turbulent transfer by analogy with the molecular transfer may be justified if account is taken of some peculiarities which will be discussed below.

Now let us consider the extent of the validity of the analogy between molecular transfer and transfer with small-scale turbulence [12].

Random molecular motion may be characterized by the mean molecular velocity  $v_m$  and the length of the mean free molecular path  $l_m$ . These quantities define the diffusion coefficient (or in



the case of heat transfer, the thermal conductivity)

$$D_m \sim v_m l_m \quad (5.1)$$

which is the proportionality factor between the flux of mass (or heat) and the gradient of its concentration (or temperature).

Similarly, the random turbulent motion may be characterized by the mean value  $v$  of the turbulent velocity fluctuations (which are a measure of the intensity of turbulence and by the turbulence scale  $l$  of the "mixing length" type introduced by Prandtl). We may define the turbulent diffusivity as

$$D_T \sim vl \quad (5.2)$$

which is the proportionality factor between the mean turbulent flow of the substance transferred and its average concentration

$$J = -D_T \rho \nabla \bar{C} \quad (5.3)$$

where

$$J = \overline{\rho C' v'} \quad (5.4)$$

(the prime indicates deviations from the mean value).

If we accept the diffusion law expressed by formula (4.3), then, using the continuity equation for the transferred substance, we obtain the ordinary (parabolic) form of the diffusion equation. However, there is a tremendous difference between the scales of motion in the molecular and turbulent processes. In molecular diffusion, for example, we have:

$$\begin{aligned} v_m &\sim 10^4 \text{ cm/s} & l_m &\sim 10^{-5} \text{ cm} \\ D_m &\sim 10^{-1} \text{ cm}^2/\text{s} & \tau_m &\sim 10^{-9} \text{ s} \end{aligned}$$

Whereas for turbulent motions the acceptable values of turbulent pulsations are  $\sim 10$  per cent of the mean velocity and lie within the range

$$v \sim 1-10^2 \text{ cm/s}, \quad l \sim 1-10^3 \text{ cm}.$$

Hence

$$\begin{aligned} D_T &\sim 1-10^5 \text{ cm}^2/\text{s} \\ \tau_r &\sim 10^{-3}-10^3 \text{ s}. \end{aligned}$$

It follows from the above estimations that, firstly, in the majority of the problems of turbulent transfer, the molecular processes may be neglected ( $D_T \gg D_m$ ).

Secondly (and this is even more important) there is a qualitative difference in the description of turbulent transfer, since because of the very large difference in the scales and velocities, the parabolic equations usually employed for the description of the molecular transfer and derived with the assumption that molecular velocity is infinite are not valid. The validity of parabolic transfer equations decreases with increasing effective velocities of the diffusing substance (or heat).

Therefore the parabolic equation of turbulent diffusion which indicates that an arbitrary disturbance will be felt, even to a very small degree, at any distance, however large, from the source, must be replaced by the hyperbolic transport equation.

Using again the equation of irreversible thermodynamics relating the fluxes and thermodynamic forces as modified above for the unsteady-state processes, we obtain for the case of isotropic turbulence

$$\tau_r \frac{\partial^2 C}{\partial \tau^2} + \frac{\partial C}{\partial \tau} = D_T \frac{\partial^2 C}{\partial y^2} \quad (5.5)$$

If  $D_T$  is variable, then the term on the right-hand side becomes of the form

$$\frac{\partial}{\partial y} \left( D_T \frac{\partial C}{\partial y} \right)$$

Equation (5.5) was derived by Goldstein [13] (see also [14]) by considering the known problem on random walks. In the same work the correlation for the case of non-isotropic turbulence is presented.

In the problem of random walks the Markovian stochastic processes of various orders may be considered.

An ordinary diffusion equation may easily be derived with the assumption that diffusing particles move at random, their co-ordinates changing in time following the law of the Markovian stochastic process of the first order. Then the diffusion equation is Kolmogorov's equation for this stochastic process.

This procedure is insufficient and too simple to be applied to turbulent transfer processes. Probability of the position of a transferred substance particle in turbulent transfer depends

at any moment  $\tau$  not only on its position in the previous moment, but on some portion of the previous path of the particle. If we restrict ourselves by the Markovian process of the second order, then a transfer equation of the hyperbolic type is obtained.

There exists another more simple derivation of hyperbolic transfer equation from a generalized equation of Focker-Plank in a phase space [15].

In conclusion it should be emphasized that equation (5.5) is hyperbolic, which shows that the term

$$\tau_r \frac{\partial^2 C}{\partial \tau^2}$$

is important irrespective of the order of its value, since it contains the higher derivative and thus determines the type of the equation which changes the character of the solution. Let us compare the behaviour of the solutions of parabolic and hyperbolic transfer equations when, for example, at the initial moment in a finite space there is a source of the form

$$C(0, y) = C_0 \delta(y). \quad (5.6)$$

We have

$$C_p(y, \tau) = \frac{C_0}{\sqrt{4\pi D_T \tau}} \exp\left(-\frac{y^2}{2D_T \tau}\right) \quad (5.7)$$

and from equation (5.5) it follows respectively

$$\left. \begin{aligned} C_h(y, \tau) &= C_0 \frac{1}{4\tau_0} e^{-\tau/2\tau_0} \left[ I_0(Y) \right. \\ &+ \left. \frac{\tau}{2\tau_r} \frac{I_1(Y)}{Y} \right] \text{ at } y < \left( \frac{D_T}{\tau_r} \right)^{\frac{1}{2}} \tau \\ C_h(y, \tau) &= 0 \text{ at } y > \left( \frac{D_T}{\tau_r} \right)^{\frac{1}{2}} \tau \end{aligned} \right\} (5.8)$$

where

$$Y = \frac{1}{2\sqrt{\tau_0}} \sqrt{\left( \frac{\tau^2}{\tau_r} - \frac{y^2}{D_T} \right)}$$

$I_0(Y)$  and  $I_1(Y)$  are the modified Bessel functions of the zeroth and first orders. With small values of time, the behaviour of solutions (5.7) and (5.8) is essentially different. It is a fundamental fact that, as it follows from equation (5.7), diffusion occurs following the law  $\sqrt{y^2} \sim \sqrt{\tau}$ ,

while from equation (5.8) we have  $\sqrt{y^2} \sim \tau$ . At  $\tau \rightarrow \infty$  (5.7) approaches asymptotically (5.8).

Some notes are given below on the possibility of the generalization of the hyperbolic transfer equations for the case of more than one-dimensional (three-dimensional) problems.

For the derivation of the equations describing transfer with the assumption of a finite propagation velocity of the substance in a three-dimensional case, an essentially more complex three- (or two-) dimensional Markovian process should be considered. We may show that the transfer equation will not be differential any more but integro-differential. The integral operator in this equation cannot always be expressed in the form of time derivatives of different orders. It may be shown (we shall not do this because of the lack of space) that in the simplest case of two-dimensional diffusion the turbulent transfer equation may be formulated as a differential equation of the type (5.5), provided only that  $\tau_r(x) - \tau_r(y)$ , which occurs, for example, in isotropic turbulence.

In conclusion, it may be pointed out that the methods of irreversible thermodynamics are of great significance for research on interconnected heat and mass transfer processes. Further development of these methods in view of their application to high-rate unsteady-state transfer processes becomes an urgent task in the general study of heat and mass transfer.

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#### APPENDIX I

The Boltzmann equation is valid for rarefied gas where only double molecular collisions are possible. With no external forces it is of the form

$$\frac{\partial f}{\partial \tau} + \vec{\xi} \frac{\partial f}{\partial \mathbf{x}} = \frac{1}{m} J_c \quad (\text{I.1})$$

Here  $f(\vec{x}, \vec{\xi}, \tau)$  is the distribution function of mass density;  $J_c$  is the integral of collisions depending on the law of molecular interaction.

Grad proposed to use the Hermite polynomial expansion of the distribution function  $f$  taking as a weight function the equilibrium Maxwellian function  $f^{(0)}$

$$f - f^{(0)} = \sum_{n=0}^{\infty} \frac{1}{n!} a_i^{(n)} H_i^{(n)} \quad (\text{I.2})$$

Substitution of this expansion into the Boltzmann equation leads to an infinite system of differential equations. The proper approxima-

tion to the complete solution of the Boltzmann equation is determined by the number of the expansion terms taken. To obtain a closed form of the final system of differential equations all Hermite coefficients of higher order are assumed to be zero.

The third approximation is studied best of all when in the distribution function three first terms are considered

$$f = f^{(0)} \sum_{i,j,k} \left( 1 + \frac{1}{2} a_{ij}^{(2)} H_{ij}^{(2)} + \frac{1}{6} a_{ijk}^{(3)} H_{ijk}^{(3)} \right) \quad (\text{I.3})$$

The Hermite coefficients  $a_{ij}^{(2)}$  and  $a_{ijk}^{(3)}$  are related to the momenta of the distribution function of the second and third order

$$a_{ij}^{(2)} = \frac{p_{ij}}{p}, \quad a_{ijk}^{(3)} = \frac{S_{ijk}}{p\sqrt{[RT]}}$$

where  $p_{ij}$  is the stress tensor. The third convolute moment  $S_i = \sum_j S_{ijj}$  which equals the doubled heat flux  $q_i$  is of important physical significance.

Therefore instead of approximation (1.3) the incomplete third approximation is used

$$f = f^{(0)} \sum_{i,j} \left( 1 + \frac{1}{2} a_{ij}^{(2)} H_{ij}^{(2)} + \frac{1}{15} a_i^{(3)} H_i^{(3)} \right), \quad (a_i = \sum_{j,k} a_{ijk}) \quad (\text{I.4})$$

which is written as

$$f = f^{(0)} \sum_{i,j} \left\{ 1 + \frac{p_{ij}}{2pRT} C_i C_j - \frac{q_i}{RT} C_i \left( 1 - \frac{C^2}{5RT} \right) \right\}, \quad (C_i = \xi_i - w_i) \quad (\text{I.5})$$

Thus the parameters of state of the system are taken to be the momentum components,  $\rho$ ,  $T$ ,  $w_i$ ,  $p_{ij}$ ,  $q_i$ ; there are all together thirteen of these. Stresses and heat fluxes are examined together with the variables  $\rho$ ,  $T$ ,  $w_i$ .

The system of equations of the 13 momenta includes equations of mass, momentum and energy conservation as well as equations for stresses and heat flux

$$\frac{\partial \rho}{\partial \tau} + \sum_r \frac{\partial}{\partial x_r} (\rho w_r) = 0 \quad (\text{I.6})$$

$$\frac{\partial w_i}{\partial \tau} + \sum_r \left( w_r \frac{\partial w_i}{\partial x_r} + \frac{1}{\rho} \frac{\partial P_{ir}}{\partial x_r} \right) = 0 \quad (\text{I.7})$$

$$\frac{\partial p}{\partial \tau} + \sum_{i,r} \left\{ \frac{\partial}{\partial x_r} (w_r p) + \frac{2}{3} P_{ir} \frac{w_i}{\partial x_r} + \frac{2}{3} \frac{\partial q_r}{\partial r x} \right\} = 0 \quad (\text{I.8})$$

$$\sum_r \frac{\partial P_{ir}}{\partial x_r} = 0 \quad (\text{I.12})$$

$$\frac{\partial p}{\partial \tau} = 0 \quad (\text{I.13})$$

$$\left. \begin{aligned} \frac{\partial p_{ij}}{\partial \tau} + \sum_{r,s} \left\{ \frac{\partial}{\partial x_r} (w_r p_{ij}) + \frac{2}{3} \left( \frac{\partial q_i}{\partial x_j} + \frac{\partial q_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial q_r}{\partial x_r} \right) + p_{ir} \frac{\partial w_j}{\partial x_r} + p_{ir} \frac{\partial w_i}{\partial x_r} - \frac{2}{3} \delta_{ij} p_{rs} \frac{\partial w_r}{\partial x_s} + p \left( \frac{\partial w_i}{\partial x_j} + \frac{\partial w_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial w_r}{\partial x_r} \right) \right\} + \beta_{\rho} p_{ij} = 0 \end{aligned} \right\} (\text{I.9})$$

$$\frac{\partial p_{ij}}{\partial \tau} + \beta_{\rho} p_{ij} = 0 \quad (\text{I.14})$$

$$\frac{\partial q_i}{\partial \tau} + \sum_r \left\{ \frac{7}{2} p_{ir} \frac{\partial RT}{\partial x_r} \right\} + \frac{5}{2} p \frac{\partial RT}{\partial x_i} + \frac{2}{3} \beta_{\rho} q_i = 0 \quad (\text{I.15})$$

Hence the pressure  $p$  is constant; stresses  $p_{ij}$  decay according to the exponential law

$$p_{ij}(\tau) = p_{ij}(0) e^{-\beta_{\rho} \tau} \quad (\text{I.16})$$

(see also Section 1).

For a heat flux we shall obtain from the latter equation

$$\left. \begin{aligned} \frac{\partial q_i}{\partial \tau} + \sum_r \left\{ \frac{\partial}{\partial x_r} (w_r q_i) + \frac{7}{2} q_r \frac{\partial w_i}{\partial x_r} + \frac{2}{3} q_r \frac{\partial w_r}{\partial x_i} + \frac{2}{3} q_i \frac{\partial w_r}{\partial x_r} + RT \frac{\partial p_{ir}}{\partial x_r} + \frac{7}{2} p_{ir} \frac{\partial RT}{\partial x_r} - \frac{p_{ir}}{\rho} \frac{\partial P_{rs}}{\partial x_r} \right\} + \frac{5}{2} p \frac{\partial RT}{\partial x_i} + \frac{2}{3} \beta_{\rho} q_i = 0 \end{aligned} \right\} (\text{I.10})$$

$$\frac{\partial q_i}{\partial \tau} + \sum_r \left\{ \frac{7}{2} p_{ir} + \frac{5}{2} p \delta_{ir} \right\} \frac{\partial RT}{\partial x_r} + \frac{2}{3} \beta_{\rho} q_i = 0 \quad (\text{I.17})$$

Another possible form of it is

$$q_i + \frac{1}{2/3\beta_{\rho}} \frac{\partial q_i}{\partial \tau} = - \sum_r \left\{ \left( \frac{1.5}{\beta_{\rho}} p_{ir} \delta_{ir} + \frac{2.1}{\beta_{\rho}} \frac{R}{\rho} p_{ir} \right) \cdot \frac{\partial T}{\partial x_r} \right\} \quad (\text{I.18})$$

where  $p_{ij} = P_{ij} - p \delta_{ij}$ .

Here  $\beta$  is the collision parameter. The equations of 13 momenta are of a hyperbolic type. The time derivative entering these equations requires definition of particular initial conditions.

In the case of slowly changing flows the dependence on the initial conditions may be neglected. The time of formation of fully-developed (quasi-equilibrium) flow is considerably shorter than the time when the system reaches the equilibrium state. In the cases when these two time scales are comparable, the flows should not be considered as developed; the time derivative should play an essential role here.

Let us consider, for example, the undeveloped heat flux in a stationary gas ( $\vec{w} = 0$ ) when  $p_{ij}$  and  $q_i$  depend solely on the time. We shall arrive at the following system of equations:

$$\frac{\partial p}{\partial \tau} = 0 \quad (\text{I.11})$$

which coincides with (3.3). The quantity  $\lambda = \frac{1.5}{\beta_{\rho}} pR/\beta_{\rho}$  is the heat-conduction coefficient which usually enters the set of equations for a continuous medium. The quantity  $1/\frac{2}{3}\beta_{\rho}$  has the meaning of a relaxation time.

## APPENDIX II

For a number of capillary-porous bodies the velocity of moisture capillary motion  $w_{\text{cap}}$  is inversely proportional to the length of the motion path  $x$ ,  $w_{\text{cap}} = (a_0/x)$ , where  $a_0$  is a certain constant which depends on the void fraction of the body, its capillary properties and the liquid viscosity. Assuming to the first approximation  $w_{\text{cap}} = w_{rm}$ , we obtain the following relation for the moisture flow

$$j = -D_m \rho_0 \frac{\partial u}{\partial x} - \frac{D_m \lambda^2}{a_0^2} \frac{\partial j}{\partial \tau} \quad (\text{II.1})$$

Using the moisture balance equation

$$\rho_0 \frac{\partial u}{\partial \tau} = - \frac{\partial j}{\partial x} \quad (\text{II.2})$$

we obtain the differential equation of moisture transfer for the mass flow under isothermal conditions in the following form

$$\frac{\partial j}{\partial \tau} + \frac{D_m}{a_0^2} x^2 \frac{\partial^2 j}{\partial \tau^2} = D_m \frac{\partial^2 j}{\partial x^2} \quad (\text{II.3})$$

Let us consider the boundary-value problem for a semi-infinite body when a constant moisture flow  $j_0$  comes through its open surface

$$j(0, \tau) = j_0 \quad j(\infty, \tau) = 0 \quad (\text{II.4})$$

$$j(x, 0) = 0 \quad \frac{\partial j(0, x)}{\partial \tau} = 0 \quad (\text{II.5})$$

The solution is found in the form

$$j(x, \tau) = j_0 f(\xi) \quad (\text{II.6})$$

where

$$\xi = 2a_0 \frac{\tau}{x^2} \quad (\text{II.7})$$

In this case we obtain the differential equation

$$(\xi^2 - 1)f''(\xi) + \left(\frac{3}{2}\xi - \frac{a_0}{2D_m}\right)f'(\xi) = 0 \quad (\text{II.8})$$

with the condition

$$f(\infty) = 1, \quad f(0) = 0, \quad f'(0) = 0 \quad (\text{II.9})$$

The solution of equation (II.8) with initial conditions (II.9) may be written as

$$\left. \begin{aligned} f(\xi) &= 0 \quad \text{at } 0 \leq \xi < 1 \\ f(\xi) &= \sqrt{\left[\frac{\pi}{2}\right]} \frac{\Gamma(\alpha + \frac{3}{4})}{\Gamma(\alpha + \frac{1}{4})} \int_1^\xi \frac{(\eta - 1)^{\alpha - \frac{1}{2}}}{(\eta + 1)^{\alpha + \frac{1}{2}}} d\eta \quad \text{at } \xi > 1 \end{aligned} \right\} (\text{II.10})$$

where

$$\alpha = \frac{a_0}{4D_m}$$

The integral entering (II.10) may be expressed by hypergeometric functions. The cases  $\alpha \gg \frac{3}{4}$  and  $\alpha \ll \frac{3}{4}$  may easily be considered and for a particular case  $\alpha = \frac{3}{4}$  we obtain

$$\left. \begin{aligned} j(x, \tau) &= j_0 \\ &\left\{ \begin{aligned} 0 &\text{ at } x^2 > 2a_0\tau \\ 1 - x \sqrt{\left[\frac{2}{x^2 + 2a_0\tau}\right]} &\text{ at } x^2 < 2a_0\tau \end{aligned} \right\} \end{aligned} \right\} (\text{II.12})$$

### APPENDIX III

The solution of the system of differential equations (4.12–4.13) with boundary conditions (4.14–4.17) and with no phase conversions ( $\epsilon = 0$ ) is of the form

$$\begin{aligned} u^* &= \frac{u - u_0}{u_a - u_0} = H(\tau^* - \xi) \left\{ \left[ 1 - \frac{LuPn}{1 - Lu} (1 - \exp[-(1 - Lu)(\tau^* - \xi)]) \right] e^{-\frac{1}{2}\xi} + \right. \\ &\left. \frac{1}{2}\xi \int_\xi^{\tau^*} \left[ 1 - \frac{LuPn}{1 - Lu} (1 - e^{-(1-Lu)(\tau^*-v)}) \right] e^{-iv} \frac{I_1\left[\frac{1}{2}\sqrt{(v^2 - \xi^2)}\right]}{\sqrt{[v^2 - \xi^2]}} dv \right\} \\ &\quad + LuPn \int_0^{\tau^*} \exp[-(1 - Lu)(\tau^* - v)] \operatorname{erfc}\left(\frac{1}{2\sqrt{v}}\right) dv \quad (\text{III.1}) \end{aligned}$$

where

$$H(\tau^*) = \begin{cases} 0 & \text{at } \tau^* < 0 \\ 1 & \text{at } \tau^* > 0 \end{cases}$$

$$\xi = x/\sqrt{D_m \tau m}$$

$I_1(v)$  is the modified Bessel function of the first order. The last summand in formula (III.1) is not zero at  $\tau^* > 0$  and governs thermal diffusion moisture transfer. If moisture is transferred at a constant temperature,  $Pn$  is zero ( $Pn = 0$ ). Then from solution (III.1) we obtain

$$u^* = H(\tau^* - \xi) \left[ e^{-\xi/2} + \right.$$

$$\left. \frac{1}{2} \xi \int_{\xi}^{\tau^*} e^{-v/2} \frac{I_1(\frac{1}{2}\sqrt{v^2 - \xi^2})}{\sqrt{v^2 - \xi^2}} dv \right] \quad (\text{III.2})$$

Solution (III.2) may be written in another form

$$u^* = H(\tau^* - \xi) \left\{ 1 - \frac{1}{\pi} \int_0^1 e^{-\tau^* z} \sin(\sqrt{z(1-z)}\xi) \frac{dz}{z} \right\} \quad (\text{III.3})$$

which is presented in Section 4 (see formula 4.18).

**Abstract**—On the basis of a phenomenological theory—the thermodynamics of irreversible processes—and using particular data of kinetic and statistic theories, a systematic description is presented of transfer phenomena: heat conduction with a finite velocity of heat propagation, relaxation of stresses in visco-elastic bodies, moisture transfer in capillary-porous bodies as well as turbulent-transfer processes. Particular solutions of a hyperbolic mass-transfer equation in porous bodies are given.

**Résumé**—Sur la base d'une théorie phénoménologique—la thermodynamique des processus irréversibles—et en employant les données particulières des théories cinétiques et statistiques, une description systématique des phénomènes de transport est présentée: la conduction de la chaleur avec une vitesse finie de propagation de la chaleur, la relaxation des contraintes dans les milieux viscoélastiques, le transport de l'humidité dans les milieux poreux-capillaires aussi bien que les processus de transport turbulent. Des solutions d'une équation hyperbolique de transport de masse dans les milieux poreux sont données.

**Zusammenfassung**—Auf Grund einer phänomenologischen Theorie—der Thermodynamik irreversibler Prozesse—und unter Benützung spezieller Daten der kinetischen und statischen Theorien wird eine systematische Beschreibung der Transportphänomene gegeben: Wärmeleitung mit endlicher Geschwindigkeit der Wärmeausbreitung, Spannungsabbau in visco-elastischen Körpern, Dampftransport in kapillar-porösen Körpern und turbulente Austauschprozesse. Partikuläre Lösungen einer hyperbolischen Stofftransportgleichung in porösen Körpern sind angegeben.