HEAT TRANSFER BETWEEN TWO FLUID PHASES

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The interface (or the surface phase) in an n-component fluid is studied on a model of the discontinuity surface in continuum. Balance equations, equations for entropy production, phenomenological equations and heat transfer equations are derived, which comprise bulk phase temperatures, the temperature of the interface (or the temperature of the surface phase), the surface heat conductivity coefficient and heat transfer coefficients as explicit quantities.

In many theoretical and technological problems in chemistry the necessity is encountered of studying transfer phenomena along and across a surface phase. In the phenomenological approach, this interface (or the surface phase) becomes a discontinuity surface, which lies inside the continuum representing the whole heterogeneous system. Common procedures, methods and results of the theory of continuum cannot be employed for the discontinuity surface or, more precisely, they are applicable only if the starting axiomatic and mathematical basis is thoroughly revised. Recently, several attempts have been made[1-5] to formulate such a new basis both from the point of view of the nonequilibrium thermodynamics and the rational thermodynamics, resp. It appears that the physically most precise work is that by Bedeaux, Albano and Mazur[6], who studied transfer phenomena at the interface between two immiscible fluids. Starting from their results, the author of this work has formulated a general mathematical[7] and axiomatic[8] basis of the nonequilibrium thermodynamics of discontinuity surfaces in continuum. In the following paragraphs, this general theory will be used for studying the heat transfer in a system containing two n-component viscous fluids or possibly two phases of one n-component fluid in the absence of chemical reactions, radiation and electromagnetic effects.

In the following paragraphs, subsequently basic balance equations among quantities on the discontinuity surface in viscoelastic medium will be derived, transformed to the problem of viscous fluid and further used to derive the balance of the internal energy. Employing the local equilibrium hypothesis, we replace in this balance the internal energy by entropy, which is a common procedure in the nonequilibrium thermodynamics. The expression for the entropy production will be obtained by comparing the resulting equation with the entropy balance and it will further be used to identify existing thermodynamic fluxes and forces. By using the linearity hypothesis and other axioms from the nonequilibrium thermodynamics, phenomenological equations will be formulated and substituted into the equation of heat continuity. Thus, an equation of heat conductivity will be obtained, which will contain as explicit variables only temperatures and material "constants".

Starting Relations

A viscous fluid can be considered as a special case of viscoelastic medium[9]. The following set of balance equations[8] is satisfied on the discontinuity surface (from now on denoted as DS) in a viscoelastic medium

$$\frac{\partial \varrho^{s}}{\partial t} + \operatorname{div} \varrho^{s}\boldsymbol{v}^{s} + \llbracket J_{N} \rrbracket = 0\,, \tag{1}$$

$$\frac{\partial \varrho^{s}_{\alpha}}{\partial t} + \operatorname{div} \varrho^{s}_{\alpha}\boldsymbol{v}^{s}_{\alpha} + \llbracket J_{\alpha N} \rrbracket = 0\,, \tag{2}$$

$$(\boldsymbol{n} \,.\, (\boldsymbol{v}^{s} - \boldsymbol{v}^{s}_{\alpha})) = 0\,,$$

$$\frac{\partial \varrho^{s}\boldsymbol{v}^{s}}{\partial t} + \operatorname{div} \{\varrho^{s}\boldsymbol{v}^{s} \otimes \boldsymbol{v}^{s} - \boldsymbol{P}^{s}\} + \llbracket J_{N}\boldsymbol{v} - \boldsymbol{p} \rrbracket = 0\,, \tag{3}$$

$$[\boldsymbol{n} \,.\, \boldsymbol{P}^{s}] = 0\,,$$

$$\boldsymbol{P}^{s} = \tilde{\boldsymbol{P}}^{s}\,, \tag{4}$$

$$\frac{\partial \varrho^{s}e^{s}}{\partial t} + \operatorname{div} \{\varrho^{s}e^{s}\boldsymbol{v}^{s} - [\boldsymbol{P}^{s} \,.\, \boldsymbol{v}^{s}] + \boldsymbol{j}^{s}_{Q}\} + \llbracket J_{N}e - (\boldsymbol{p} \,.\, \boldsymbol{v}) + j_{QN} \rrbracket = 0\,, \tag{5}$$

$$(\boldsymbol{n} \,.\, \{[\boldsymbol{P}^{s} \,.\, \boldsymbol{v}^{s}] - \boldsymbol{j}^{s}_{Q}\}) = 0\,,$$

$$\frac{\partial \varrho^{s}s^{s}}{\partial t} + \operatorname{div} \{\varrho^{s}s^{s}\boldsymbol{v}^{s} + \boldsymbol{j}^{s}_{s}\} - \sigma^{s} + \llbracket J_{N}s + j_{SN} \rrbracket = 0\,, \tag{6}$$

$$(\boldsymbol{n} \,.\, \boldsymbol{j}^{s}_{s}) = 0\,,$$

where $\llbracket\;\rrbracket$ denotes the jump of the enclosed quantity at DS: $\llbracket Y \rrbracket = Y^{+} - Y^{-}$ (Y^{+} or Y^{-} is the quantity measured in the bulk phase at the positive or negative side of DS), the subscript N(T) denotes the normal (tangential) component of a vector, $\boldsymbol{n}$ is unit outer normal to DS (in our case it is oriented from the negative to the positive side of DS), $\varrho^{s}(\varrho^{\pm})$ is the surface (volume) density of the mixture – dim. ML^{-2}

(ML^{-3}) (where M is mass, L length, T time and τ temperature), $\varrho^s_\alpha(\varrho^\pm_\alpha)$ is the surface (volume) density of component α – dim. ML^{-2} (ML^{-3}), $\boldsymbol{v}^s$ $(\boldsymbol{v}^\pm)$ is the barycentric surface (volume) velocity – dim. LT^{-1} (LT^{-1}), $\boldsymbol{v}^s_\alpha$ $(\boldsymbol{v}^\pm_\alpha)$ is the surface (volume) velocity of component α – dim. LT^{-1} (LT^{-1}), $\boldsymbol{J}^\pm$ is the interphase mass flux of the mixture:

$$\boldsymbol{J}^\pm = \varrho^\pm(\boldsymbol{v}^\pm - \boldsymbol{v}^s)\,, \tag{7}$$

$\boldsymbol{J}^\pm_\alpha$ is the interphase mass flux of component α:

$$\boldsymbol{J}^\pm_\alpha = \varrho^\pm_\alpha(\boldsymbol{v}^\pm_\alpha - \boldsymbol{v}^s) \tag{8}$$

$\boldsymbol{P}^s$ $(\boldsymbol{P}^\pm)$ is the "surface" ("volume") stress tensor – dim. MT^{-2} $(ML^{-1}\,T^{-2})$, which is given by

$$\boldsymbol{P}^s = {}_R\boldsymbol{P}^s + {}_D\boldsymbol{P}^s\,, \quad \boldsymbol{P}^\pm = {}_R\boldsymbol{P}^\pm + {}_D\boldsymbol{P}^\pm\,, \tag{9}$$

where the subscript $R_{(D)}$ denotes the reversible (dissipative) part of the tensor, $\boldsymbol{p}^\pm = [\boldsymbol{n}\,.\,\boldsymbol{P}^\pm]$ is the stress vector, ~ denotes the transposed tensor, e^s $(e^\pm)$ is the specific total surface (volume) energy:

$$e^s = \tfrac{1}{2}(\boldsymbol{v}^s)^2 + u^s\,, \quad e^\pm = \tfrac{1}{2}(\boldsymbol{v}^\pm)^2 + u^\pm\,, \tag{10}$$

u^s $(u^\pm)$ is the specific surface (volume) internal energy – dim. L^2T^{-2}), $\boldsymbol{j}^s_Q$ $(\boldsymbol{j}^\pm_Q)$ is the "surface" ("volume") heat flux – dim. MLT^{-3} (MT^{-3}), s^s $(s^\pm)$ is the specific surface (volume) entropy – dim. $L^2T^{-2}\,\tau^{-1}$ $(L^2T^{-2}\,\tau^{-1})$, $\boldsymbol{j}^s_s$ $(\boldsymbol{j}^\pm_s)$ is the "surface" ("volume") flux of entropy – dim. $MLT^{-3}\,\tau^{-1}$ $(MT^{-3}\,\tau^{-1})$:

$$\boldsymbol{j}^s_s = \frac{1}{T^s}\,(\boldsymbol{j}^s_Q - \sum_\alpha \mu^s_\alpha \boldsymbol{j}^s_\alpha)\,, \tag{11}$$

$$\boldsymbol{j}^\pm_s = \frac{1}{T^\pm}\,(\boldsymbol{j}^\pm_Q - \sum_\alpha \mu^\pm_\alpha \boldsymbol{j}^\pm_\alpha)\,,$$

T^s $(T^\pm)$ is the surface (volume) temperature, μ^s_α $(\mu^\pm_s)$ is the surface (volume) chemical potential – dim. L^2T^{-2} (L^2T^{-2}), $\boldsymbol{j}^s_\alpha$ $(\boldsymbol{j}^\pm_\alpha)$ is the "surface" ("volume") diffusion flux:

$$\boldsymbol{j}^s_\alpha = \varrho^s_\alpha(\boldsymbol{v}^s_\alpha - \boldsymbol{v}^s)\,, \tag{12}$$

$$\boldsymbol{j}^\pm_\alpha = \varrho^\pm_\alpha(\boldsymbol{v}^\pm_\alpha - \boldsymbol{v}^\pm)\,,$$

σ^s is the surface entropy production – dim. $MT^{-3}\,\tau^{-1}$, (.) denotes the scalar product of two vectors, is the dyadic product of two vectors, [.] is the product of a vector and a tensor and (:) is the scalar product of two tensors.

Eqs (*1*), $(2)_1$, $(3)_1$, (*4*), $(5)_1$, $(6)_1$ are balance equations of the mass of the mixture, the mass of the component, the momentum of the mixture, the moment of momentum of the mixture, the total energy of the mixture and the entropy of the mixture, resp. (symbol $(2)_1$ refers to the first equation from the set denoted as (*2*) *etc.*). Conditions $(2)_2$, $(3)_2$, $(5)_2$, $(6)_2$, which follow from the generalized integral theorems[8], guarantee that the surface quantities are defined at (two-dimensional) DS. From condition $(2)_2$ and from definition $(12)_1$ it follows that

$$(\boldsymbol{n} \cdot \boldsymbol{j}^{s}_{\alpha}) = 0\,, \tag{13}$$

and from conditions $(3)_2$, (*4*), $(5)_2$:

$$(\boldsymbol{n} \cdot \boldsymbol{j}^{s}_{Q}) = 0\,. \tag{14}$$

If we define the "surface" material derivative by

$$\frac{^{s}\mathrm{d}*}{\mathrm{d}t} = \frac{\partial *}{\partial t} + (\boldsymbol{v}^{s} \cdot \operatorname{grad} *) \tag{15}$$

(where the symbol $*$ represents an arbitrary variable), then we obtain from balance (*1*) for an arbitrary quantity X^s the relation

$$\frac{\partial \varrho^{s} X^{s}}{\partial t} + \operatorname{div} \varrho^{s} X^{s} \boldsymbol{v}^{s} = \varrho^{s} \frac{^{s}\mathrm{d}X^{s}}{\mathrm{d}t} - X^{s}[\![J_{N}]\!]\,. \tag{16}$$

The mass balance equation of the mixture, (*1*), can be transformed to the form of the balance equation of the specific area of DS. It holds

$$b = (\varrho^{s})^{-1}\,, \tag{17}$$

where b is the specific area. From Eqs (*1*), (*17*) it follows

$$\operatorname{div} \boldsymbol{v}^{s} = b^{-1} \frac{^{s}\mathrm{d}b}{\mathrm{d}t} - b[\![J_{N}]\!]\,. \tag{18}$$

Balance equation (*2*) can be rearranged to read

$$\varrho^{s} \frac{^{s}\mathrm{d}c^{s}_{\alpha}}{\mathrm{d}t} + \operatorname{div} \boldsymbol{j}^{s}_{\alpha} + [\![J_{\alpha N}]\!] - c^{s}_{\alpha}\,[\![J_{N}]\!] = 0\,, \tag{19}$$

where $c^{s} = \varrho^{s}_{\alpha}/\varrho^{s}$ is the mass fraction.

From relations (*1*), (*2*)$_1$, and (*19*) (and from the superposition principle) it follows

$$\varrho^{s} = \sum_{\alpha} \varrho_{\alpha}^{s} , \quad \varrho^{s} \boldsymbol{v}^{s} = \sum_{\alpha} \varrho_{\alpha}^{s} \boldsymbol{v}_{\alpha}^{s} ,$$

$$\sum_{\alpha} \llbracket J_{\alpha N} \rrbracket = \llbracket J_{N} \rrbracket , \quad \sum_{\alpha} \boldsymbol{j}_{\alpha}^{s} = 0 . \tag{20}$$

Performing the scalar multiplication of Eq. (*3*)$_1$ by velocity $\boldsymbol{v}^s$, we obtain the balance of the kinetic energy. By subtracting it from Eq. (*5*)$_1$, the following relation results

$$\frac{\partial \varrho^{s} u^{s}}{\partial t} + \operatorname{div} \{\varrho^{s} u^{s} \boldsymbol{v}^{s} + \boldsymbol{j}_{Q}^{s}\} - (\boldsymbol{P}^{s} : \operatorname{grad} \boldsymbol{v}^{s}) +$$

$$+ \llbracket J_{N}\{u + \tfrac{1}{2}(\boldsymbol{v} - \boldsymbol{v}^{s})^{2}\} - (\boldsymbol{p} \,.\, (\boldsymbol{v} - \boldsymbol{v}^{s})) + j_{QN} \rrbracket = 0 \tag{21}$$

which is the balance equation of the internal energy.

In the axiomatic structure of the nonequilibrium thermodynamics, balance (*21*) is supplemented with an equation expressing the local equilibrium hypothesis. In the case of a DS in a viscoelastic mixture, this hypothesis is represented by the relations[8]

$$\varrho^{s} \frac{{}^{s}\mathrm{d}u^{s}}{\mathrm{d}t} - \varrho^{s} T^{s} \frac{{}^{s}\mathrm{d}s^{s}}{\mathrm{d}t} - ({}_{R}\boldsymbol{P}^{s} : \operatorname{grad} \boldsymbol{v}^{s}) - \varrho^{s} \sum_{\alpha} \mu_{\alpha}^{s} \frac{{}^{s}\mathrm{d}c_{\alpha}^{s}}{\mathrm{d}t} -$$

$$\llbracket ({}_{R}\boldsymbol{p} \,.\, (\boldsymbol{v} - \boldsymbol{v}^{s})) \rrbracket + \llbracket J_{N}(u - Ts - \sum_{\alpha} c_{\alpha} \mu_{\alpha}) \rrbracket -$$

$$- \llbracket J_{N} \rrbracket (u^{s} - T^{s} s^{s} - \sum_{\alpha} c_{\alpha}^{s} \mu_{\alpha}^{s}) = 0 , \tag{22}$$

$$T^{s} = T^{+} = T^{-} , \quad \mu_{\alpha}^{s} = \mu_{\alpha}^{+} = \mu_{\alpha}^{-} ,$$

$$\operatorname{div}_{R} \boldsymbol{P}^{s} = - \llbracket {}_{R}\boldsymbol{p} \rrbracket , \quad (\boldsymbol{n} \,.\, [{}_{R}\boldsymbol{P}^{s} \,.\, \boldsymbol{v}^{s}]) = 0 .$$

Equation of Heat Conduction in a Viscous Fluid

From a formal point of view, the model of viscoelastic medium differs from that of viscous fluid only in the expression of the reversible part of the stress tensor. In the case investigated it holds

$${}_{R}\boldsymbol{p}^{\pm} = -\boldsymbol{n} \not{p}^{\pm} , \quad {}_{R}\boldsymbol{P}^{s} = (\boldsymbol{1} - \boldsymbol{n} \otimes \boldsymbol{n}) \gamma , \tag{23}$$

where $\wp^{\pm}$ is pressure in the bulk phase, γ is surface tension and $\mathbf{1}$ is unit tensor. At a thermodynamic equilibrium, we can also use the relations

$$u - Ts - \sum_{\alpha} c_{\alpha}\mu_{\alpha} + \wp v = 0\,,$$

$$u^{s} - T^{s}s^{s} - \sum_{\alpha} c^{s}_{\alpha}\mu^{s}_{\alpha} - \gamma b = 0\,, \tag{24}$$

where $v = \varrho^{-1}$ is specific volume.

Substituting relations (*7*), (*16*), (*18*) and (*23*) into Eq. (*21*), we obtain the balance equation of the internal energy at DS in a viscous n-component fluid:

$$\varrho^{s}\frac{{}^{s}\mathrm{d}u^{s}}{\mathrm{d}t} - u^{s}[\![J_{\mathrm{N}}]\!] + \operatorname{div}\dot{j}^{s}_{\mathrm{Q}} - ({}_{\mathrm{D}}\boldsymbol{P}^{s} : \operatorname{grad}\boldsymbol{v}^{s}) - \gamma\varrho^{s}\frac{{}^{s}\mathrm{d}b}{\mathrm{d}t} + \gamma b[\![J_{\mathrm{N}}]\!] +$$

$$+ [\![J_{\mathrm{N}}\{u + \wp v + \tfrac{1}{2}(\boldsymbol{v} - \boldsymbol{v}^{s})^{2}\} - ({}_{\mathrm{D}}\boldsymbol{p}\,.\,(\boldsymbol{v} - \boldsymbol{v}^{s})) + \dot{j}_{\mathrm{QN}}]\!] = 0\,. \tag{25}$$

Here, $\boldsymbol{P}^{s}$ $({}_{\mathrm{D}}\boldsymbol{P}^{\pm})$ corresponds to the viscous part of the surface (volume) stress tensor and ${}_{\mathrm{D}}\boldsymbol{p}^{\pm} = [\boldsymbol{n}\,.\,{}_{\mathrm{D}}\boldsymbol{P}^{\pm}]$.

Similarly, if we rearrange the local equilibrium equation $(22)_1$ with the help of relations (*7*), (*16*), (*18*), (*23*), (*24*), we obtain

$$\varrho^{s}\frac{{}^{s}\mathrm{d}u^{s}}{\mathrm{d}t} - \varrho^{s}T^{s}\frac{{}^{s}\mathrm{d}s^{s}}{\mathrm{d}t} - \varrho^{s}\gamma\frac{{}^{s}\mathrm{d}b}{\mathrm{d}t} - \varrho^{s}\sum_{\alpha}\mu^{s}_{\alpha}\frac{{}^{s}\mathrm{d}c^{s}_{\alpha}}{\mathrm{d}t} = 0\,. \tag{26}$$

Now, if we rearrange Eq. (*26*) with the help of relations (*7*), (*8*), (*12*), (*19*), (*20*), (*24*) and $(22)_{2,3}$ and insert the result into balance (*25*), we have

$$\varrho^{s}\frac{{}^{s}\mathrm{d}s^{s}}{\mathrm{d}t} - s^{s}[\![J_{\mathrm{N}}]\!] + \operatorname{div}\frac{1}{T^{s}}\{\dot{j}^{s}_{\mathrm{Q}} - \sum_{\alpha}\dot{j}^{s}_{\alpha}\mu^{s}_{\alpha}\} +$$

$$+ (\dot{j}^{\alpha}_{\mathrm{Q}}\,.\,(T^{s})^{-2}\operatorname{grad}T^{s}) + \sum_{\alpha}(\dot{j}^{s}_{\alpha}\,.\operatorname{grad}\mu^{s}_{\alpha}(T^{s})^{-1}) -$$

$$- \frac{1}{T^{s}}({}_{\mathrm{D}}\boldsymbol{P}^{s} : \operatorname{grad}\boldsymbol{v}^{s}) + \frac{1}{T^{s}}[\![\mathscr{j}_{\mathrm{QN}} - \sum_{\alpha}\mathscr{j}_{\alpha\mathrm{N}}\mu_{\alpha} +$$

$$+ J_{\mathrm{N}}\tfrac{1}{2}(\boldsymbol{v} - \boldsymbol{v}^{s})^{2} - ({}_{\mathrm{D}}\boldsymbol{p}\,.\,(\boldsymbol{v} - \boldsymbol{v}^{s}))]\!] + [\![J_{\mathrm{N}}s]\!] = 0\,. \tag{27}$$

By comparing balance *(6)*$_1$ and relation *(27)* (see also *(11)*, *(15)*, *(16)*), it is obvious that the entropy production assumes the form

$$\sigma^s = (T^s)^{-1} ({}_D\boldsymbol{P}^s : \text{grad } \boldsymbol{v}^s) + (T^s)^{-1} \llbracket ({}_D\boldsymbol{p} \cdot (\boldsymbol{v} - \boldsymbol{v}^s)) \rrbracket - $$
$$- (\boldsymbol{j}^s_Q \cdot (T^s)^{-2} \text{ grad } T^s) - \sum_\alpha (\boldsymbol{j}^s_\alpha \cdot \text{grad } \mu^s_\alpha (T^s)^{-1}) +$$
$$+ \left\llbracket \{ j_{QN} - \sum_\alpha \mu_\alpha j_{\alpha N} \} \left(\frac{1}{T} - \frac{1}{T^s} \right) \right\rrbracket - (T^s)^{-1} \llbracket J_N \tfrac{1}{2} (\boldsymbol{v} - \boldsymbol{v}^s)^2 \rrbracket \,. \qquad (28)$$

In the following we shall limit ourselves to the problem of "pure" heat conduction along and across the DS. Therefore we can assume that

$$\boldsymbol{v}^+ = \boldsymbol{v}^- = \boldsymbol{v}^+_\alpha = \boldsymbol{v}^-_\alpha = \boldsymbol{v}^s = 0 \,. \qquad (29)$$

In this case, relation *(28)* reduces to

$$\sigma^s = -(\boldsymbol{j}^s_Q \cdot (T^s)^{-2} \text{ grad } T^s) +$$
$$+ \llbracket j_{QN} \rrbracket \left\{ \left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s} \right\} + \langle j_{QN} \rangle \left\llbracket \frac{1}{T} \right\rrbracket , \qquad (30)$$

where $\langle\ \rangle$ denotes the "mean value" of a quantity at DS: $\langle Y \rangle = \frac{1}{2}(Y^+ + Y^-)$. In agreement with condition *(14)*, only the tangential component of heat flux is present in the first term of Eq. *(30)*. Because of that, the scalar product is affected only by the tangential component of the temperature gradient. The flux $\boldsymbol{j}^s_Q$ possesses a vector character and it follows from condition *(14)* that its direction is parallel with the DS. The remaining two scalar fluxes, $\llbracket j_{QN} \rrbracket$ and $\langle j_{QN} \rangle$, pass through the interface.

It has been shown in ref.[8] that axioms from the nonequilibrium (Onsager) thermodynamics can be used even in the case of a two-dimensional region. From the linearity principle and from the principles of material and time reversal invariance it follows

$$\boldsymbol{j}^s_{QT} = -\lambda^s (\text{grad } T^s)_T ,$$
$$\llbracket j_{QN} \rrbracket = L_1 \left\{ \left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s} \right\} + L_2 \left\llbracket \frac{1}{T} \right\rrbracket ,$$
$$\langle j_{QN} \rangle = L_2 \left\{ \left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s} \right\} + L_3 \left\llbracket \frac{1}{T} \right\rrbracket , \qquad (31)$$

where λ^s is the surface heat conductivity coefficient and L_1, L_2, L_3 are heat transfer coefficients.

A natural consequence of assumptions (*29*) is a constant magnitude of the material volume and of the interfacial area. Further it follows from Eqs (*29*) and (*15*) that ${}^s\mathrm{d}*/\mathrm{d}t = \partial*/\partial t$. By taking into account that under these assumptions it holds

$$ {}^s\mathrm{d}\, u^s/\mathrm{d}t = c^s\, \partial T^s/\partial t\,, $$

(where c^s is the "surface" specific heat at constant volume and area), Eq. (*25*) assumes the form

$$ \varrho^s c^s \frac{\partial T^s}{\partial t} + \operatorname{div} j^s_Q + [\![j_{QN}]\!] = 0\,. \tag{32} $$

Now, if we insert phenomenological equations $(31)_{1,2}$ into relation (*32*), we obtain

$$ \frac{\partial T^s}{\partial t} - a^s\, \Delta T^s + L_1^* \left\{ \left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s} \right\} + L_2^* \left[\!\!\left[\frac{1}{T} \right]\!\!\right] = 0\,, \tag{33} $$

where $a^s = \lambda^s/\varrho^s c^s$ is the surface temperature conductivity coefficient, $L^*_{1,2} = L_{1,2}/\varrho^s c^s$ are reduced heat transfer coefficients and Δ is the Laplace operator.

DISCUSSION

Let us first try to explain the meaning of the surface quantities. The following basic model concept was employed in[6-8]. Let us have a time-dependent material volume $V(t)$, which is divided by the discontinuity surface $B(t)$ into two parts (phases) $V_{\mathrm{I}}(t)$ and $V_{\mathrm{II}}(t)$. The motion of area $B(t)$ is represented by the relation $f(\boldsymbol{r}, t) = 0$ (where $\boldsymbol{r}$ is the position vector). Consequently, phase V_{I} corresponds to the region $f(\boldsymbol{r}, t) > 0$ and phase V_{II} to $f(\boldsymbol{r}, t) < 0$.

If a certain local property X (an intensive parameter) of a material is measured, the value $X^+(\boldsymbol{r}, t)$ is obtained at position $\boldsymbol{r}$ in the region $f > 0$, $X^-(\boldsymbol{r}, t)$ for $\boldsymbol{r}$ in the region $f < 0$ and, finally, the surface property $X^s(\boldsymbol{r}, t)$ for positions on the surface $B(t)$ *i.e.*, for $\boldsymbol{r}$ in the region $f(\boldsymbol{r}, t) = 0$. Summarizing it, we can write

$$ X = X^+ \vee X^- \vee X^s\,, $$

where $\vee$ denotes disjunction. In other words, the surface quantities are identical with those which would actually be measured by a local probe on the area $B(t)$. Differences between dimensions of some properties of the same type are also determined by the method of measurement. For example, $\varrho^{\pm}$ is measured in accordance with the condition

$$\varrho^{\pm} = \lim_{\Delta V_{\mathrm{I,II}} \to \mathrm{P}} \frac{\Delta M}{\Delta V_{\mathrm{I,II}}}$$

whereas for ϱ^{s} it holds

$$\varrho^{\mathrm{s}} = \lim_{\Delta B \to \mathrm{Q}} \frac{\Delta M}{\Delta B} ,$$

where ΔM is mass and $P(Q)$ denotes a certain point in the volume (on the surface).

Conditions of the type $(\boldsymbol{n} \,.\, \boldsymbol{X}^{\mathrm{s}}) = 0$ (or $[\boldsymbol{n} \,.\, \boldsymbol{X}^{\mathrm{s}}] = 0$) – *e.g.*, $(2)_2$, $(3)_2$, $(5)_2$ *etc.* – guarantee that in a special coordinate system (with one axis oriented along $\boldsymbol{n}$) all surface vector and tensor properties (except $\boldsymbol{v}^{\mathrm{s}}$) reduce to two-component vectors and to two-by-two matrix tensors. This reduction corresponds also with the reduction of vector differential operations (for more details see, ref.[10]).

Now let us turn back to the problem of heat conduction through the interface, which is, in the system investigated, represented by Eq. (*33*), where the nonlinear source term, *i.e.*,

$$L_1^* \left\{ \left\langle \frac{1}{T} \right\rangle - \frac{1}{T^{\mathrm{s}}} \right\} + L_2^* \left[\!\!\left[\frac{1}{T} \right]\!\!\right]$$

corresponds directly with temperature differences between the volume and surface phases.

There are two special cases which are significant practically:

a) *the Waldmann approximation*:

$$\left\langle \frac{1}{T} \right\rangle = \frac{1}{T^{\mathrm{s}}} .$$

In this case, the second term in relation (*30*) is equal to zero and the phenomenological equations reduce to the form

$$\boldsymbol{j}_{\mathrm{QT}}^{\mathrm{s}} = -\lambda^{\mathrm{s}}(\mathrm{grad}\ T^{\mathrm{s}})_{\mathrm{T}} , \quad \langle j_{\mathrm{QN}} \rangle = L_3 [\![T^{-1}]\!] . \qquad (34)$$

Eq. $(34)_2$ is practically identical with Newton's cooling law. Relation (*33*) is in this case reduced to the usual parabolic equation.

b) *Constant surface temperature*: $T^{\mathrm{s}}(r, t) = \mathrm{const.}$ At this condition, it follows from Eq. (*33*) that

$$L_1^*/L_2^* = \langle T \rangle \left([\![T]\!] \right)^{-1} + \left(T^{\mathrm{s}} [\![(T)^{-1}]\!] \right)^{-1} .$$

Finally we would like to point to a certain ambiguousness in the expression for the entropy production, σ^s, which is determined by conditions $(22)_{2,3}$. In this paper we employed the relation ((Eqs (*19*), $(22)_3$))

$$\varrho^s \sum_\alpha \mu_\alpha^s \frac{{}^s\mathrm{d}c_\alpha^s}{\mathrm{d}t} = \sum_\alpha \mu_\alpha^s (c_\alpha^s [\![J_N]\!] - \operatorname{div} j_\alpha^s) - \sum_\alpha [\![J_{\alpha N}]\!] \langle \mu_\alpha \rangle$$

for the modification of the local equilibrium (*26*). However, equally well we coul write

$$\varrho^s \sum_\alpha \mu_\alpha^s \frac{{}^s\mathrm{d}c_\alpha^s}{\mathrm{d}t} = \sum_\alpha \mu_\alpha^s (c_\alpha^s [\![J_N]\!] - \operatorname{div} j_\alpha^s) - \sum_\alpha [\![J_{\alpha N}]\!] \mu_\alpha^s .$$

This second method was discussed in[8] and it gave the entropy production where, besides the terms known from Eq. (*28*), there are also *n* scalar forces $-(T^s)^{-1} . (\langle \mu_\alpha \rangle - \mu_\alpha^s)$ and *n* conjugated fluxes $[\![J_{\alpha N}]\!]$, which – due to condition $(20)_3$ – are not fully independent.

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