1. Introduction.

Both classical and modern thermodynamics are based on two fundamental laws, the first and the second law of thermodynamics. The first law declares the conservation of the energy. Its content is clear and widely accepted and is seldom doubted. The situation is completely different with the second law. It has several formulation, and is often doubted, nevertheless, every one is aware of the losses of disposable energy. To discuss the several opinions about the formulation of the second law is far beyond the scope of this lecture, so the common is stressed. All the thermodynamic theories are utilizing that the entropy of any adiabatically closed system is increasing if anything happens in it. But what does it mean that the system is adiabatically closed, and what to do if it is not. Heat is newer defined (it is a “primitive idea”) and one is faced with a rather complicated problem if several kind of transports are present. What part of the energy transport is work and what part is heat?
The above formulation of the problem is difficult and we may obtain some ease if focusing on the transport of the entropy. In classical irreversible thermodynamics, the relation between heat flow and entropy flow

\[ J_s = \frac{1}{T} J_q \]

is presumed. Here we put aside the question what \( J_q \) is. It is assumed the flow density in the balance equation for the internal energy, which reads

\[ \rho \frac{d\dot{u}}{dt} + \text{div} J_q = \sigma_u. \]

For the derivation of the balance equation of the entropy, the equilibrium form of the entropy function is also presumed in classical irreversible thermodynamics. The two presumptions are supported by the hypothesis of local equilibrium.

If local equilibrium is departed from, the question if the coefficient of the heat flow in equation (1) equals the partial derivative of the entropy with respect to the internal energy emerges. The formula (1) is modified even in a local equilibrium system by the diffusion. Instead of equation (1),

\[ J_s = \frac{1}{T} J_q - \sum_i \frac{\mu_i}{T} J_i \]

holds. Out of local equilibrium, the coefficients of the current densities are uncertain, their actual values depend on the choice of the dynamic variables. The ambiguity is stopped by the canonical representation of the dynamic degrees of freedom;

\[ \frac{1}{T} = \frac{\delta s}{\delta u} = \frac{\delta s_0}{\delta u}, \quad \frac{\mu_i}{T} = \frac{\delta s}{\delta c_i} = \frac{\delta s_0}{\delta c_i} \]

This assumption – i.e. to postulate the validity of equation (3) – is, however, quite arbitrary, and its correctness is proved
merely by the practical applicability of the relationships derived from it.

In what follows, we shall examine what consequences result from the rejection of the above hypothesis. For simplicity, again the model of heat conduction in solid bodies will be used for this purpose, however, it should be emphasized that this is only in order to simplify the calculations and considerations, and that there is no difficulty in the simultaneous consideration of various transport processes in a completely general manner.

Let us take a solid body with specific internal energy as the only equilibrium state parameter, but in which the processes are to be characterised by dynamic variables. According to the Morse lemma, the entropy may be given by

\[ s = s_0(u) - \frac{1}{2} \sum_i \xi_i^2 \]  

(5)

In the general form of the entropy balance \( J_s \) may differ from the usual form \( J_s = \frac{1}{T} J_q \) and be

\[ J_s = \frac{1}{T} J_q + K, \]  

(6)

where vector \( K \) expresses the deviation from the formula valid in local equilibrium. Equation (6) is regarded as the definition for the vector \( K \). Müller was the first who presumed the existence of the vector \( K \). In extended thermodynamics, it is a “constitutive quantity”.

\( K \) is obviously zero in all cases when the medium is in a local equilibrium, hence \( K \) is zero if all the dynamic variables disappear. Based on this, \( K \) may be put into the form

\[ K = - \sum_i J_i \xi_i \]  

(7)

where the quantities \( J_i \) introduced here depend on the same variables as vector \( K \) and they are continuous if \( K \) is
continuously differentiable. Dynamic coordinates $\xi_i$ are treated here as if they were scalar quantities but they can also be components of tensors of different orders. Entropy production can be obtained in the usual way by comparing equations (1), (2), (5), (6) and (7):

$$\sigma_s = \rho \left( \frac{1}{T} \dot{u} - \sum \xi_i \xi_i \right) + \frac{1}{T} \text{div } J_q +$$

$$+ J_q \text{grad } \frac{1}{T} - J_i \text{grad } \xi_i - \xi_i \text{div } J_i$$

(8)

Let us now utilize the balance equation of internal energy given in equation (2) and rearrange the equation into the form

$$\sigma_s = J_q \text{grad } \frac{1}{T} - \sum J_i \text{grad } \xi_i - \sum \xi_i (\rho \xi_i + \text{div } J_i)$$

(9)

We do not write the linear laws, although, they are very important for applications. For the interpretation of the result derived, let us introduce correlation

$$\rho \xi_i + \text{div } J_i = \sigma_{\xi_i}$$

(10)

which is apparently the balance equation of a certain extensive quantity. If this extensive quantity $\Xi_i$ is defined as

$$\Xi_i = \int V \rho \xi_i dV$$

(11)

then it is obvious that vector $J_i$ can be interpreted as the current density of the transport of extensive quantity $\Xi_i$. The form of entropy current density (6) is written as

$$J_s = \frac{\partial s}{\partial u} J_q + \sum \frac{\partial s}{\partial \xi_i} J_i$$

(12)

which may be considered the natural generalization of the classical equation (3). Constitutive equations describing transport
and source densities can be determined on the basis of the actual expression of entropy production. (In linear theories, based on the forms of Onsager's linear laws, in non-linear theories according to those corresponding to the former.)

The ideas presented may be generalized further. The validity of equation (3) in a local equilibrium is not guaranteed unless it is involved into the definition of local equilibrium.

If not doing so, Müller's $K$ vector may differ from zero even in a local equilibrium state. Next we follow Nyfri's argumentation.

The entropy is not a primitive quantity its transport is a result of the transport of the extensive quantities. It vanishes when all other transports do. From here the relation

$$K = \sum B_i J_i$$

follows, where the tensorial order of the quantities $B_i$ are one higher than that of $J_i$'s.

The determination of the quantities $B_i$ belongs to constitutive modeling. They do not vanish even in the linear approximation. To see the consequences of the general hypothesis the heat conduction is taken for an example.

The balance equation for a simple model reads

$$\rho \dot{u} + \text{div} J_q = 0;$$

the entropy function is taken

$$s = s_0(u)$$

according to the hypothesis of local equilibrium. The entropy current is joined to the heat flow by eq. (6) where the $K$ vector is determined by

$$K = BJ_q$$

in agreement with eq. (13).
The entropy production density reads

\[
(17) \quad \sigma_s = J_q \text{grad} \frac{1}{T} + B^T : \text{Grad} J_q + J_q \text{Div} B^T.
\]

From here the constitutive equations describing the processes in linear order are determined as

\[
J_q = L_0 \left( \text{grad} \frac{1}{T} + \text{Div} B^T \right)
\]

\[
(18) \quad B^T = L_1 \text{Grad} J_q + L_2 (\text{Grad} J_q)^T + L_3 \text{div} J_q
\]

where \( \delta \) is the unite tensor and \( L_0, L_1, L_2 \) and \( L_3 \) are the phenomenological coefficients obeying the inequalities

\[
L_0 > 0; \ L_1 > |L_2|; \ L_3 > -\frac{L_1 + L_2}{6},
\]

expressing the second law. Eliminating the tensor \( B \) from the equations we get the correlation determining the heat flow;

\[
(19) \quad J_q = L_0 \text{grad} \frac{1}{T} + L_0 [L_1 \Delta J_q + (L_2 + L_3) \text{grad} \text{div} J_q].
\]

As the \( L \) coefficients may depend on the temperature, it is convenient to introduce new ones:

\[
\lambda = \frac{L_0}{T^2}; \ C_1 = L_0 L_1; \ C_2 = L_0 (L_2 + L_3)
\]

with which equation (19) transforms into

\[
(20) \quad J_q = -\lambda \text{grad} T + C_1 \Delta J_q + C_2 \text{grad} \text{div} J_q.
\]

The heat flow is not determined by the temperature distribution alone but the boundary conditions are also of importance. It is to be investigated if the role of the boundary conditions yield something not acceptable. For small amplitude
oscillations the coefficients $\lambda$, $C_1$, $C_2$ are constant so the equation for the temperature reads

\begin{equation}
\rho \ddot{u} = \lambda \Delta T + (C_1 + C_2) \Delta(\rho \dot{u}),
\end{equation}

which takes the form

\begin{equation}
\rho c \dot{T} = \lambda \Delta T + (C_1 + C_2) \Delta(\rho c \dot{T})
\end{equation}

if the specific heat $c$ is introduced. With a proper choice of the units of length and time the equation reduces to

\begin{equation}
\dot{T} \Delta T + \Delta \dot{T}.
\end{equation}

The dispersion relation for plane waves of form

\begin{equation}
T = Ae^{i(kr - \omega t)},
\end{equation}

reads

\begin{equation}
i\omega = \frac{k^2}{1 + k^2},
\end{equation}

from which a lot of interesting consequences come. The fine enough patterns do not change shape while decreasing in amplitude. On the other side, the wave length for real frequencies has a minimum. The real part and the imaginary part of the wave number is plotted against the real frequency in the figure. It looks like as if the purely phenomenological considerations displaced the molecular structure of the material.
And now a comment. The equation (23) results also from a model supposing that the local state is determined by the internal energy and the gradient of the temperature (or of the reciprocal temperature). In quadratic approximation the entropy function may be cast into the form

\[ s = s_0 \left[ u - \frac{\gamma}{2} \left( \frac{\text{grad} \frac{1}{T}}{T} \right)^2 \right] \]

Supposing the classical formula (1) for the entropy current, we get for the entropy production density

\[ \sigma_s = \frac{\text{grad} \frac{1}{T}}{T} \left( J_q - \rho \frac{1}{T} \gamma \frac{d}{dt} \frac{1}{T} \text{grad} \frac{1}{T} \right). \]  

The linear equation reads

\[ J_q = L_0 \text{grad} \frac{1}{T} + \rho \frac{1}{T} \gamma \frac{d}{dt} \text{grad} \frac{1}{T} \]
The constitutive equation reduces to

\[
J_\eta = -\lambda \text{grad } T - \frac{\rho \gamma}{T^3} \text{grad } \dot{T}
\]

for small amplitude processes. Here the heat conductivity \( \lambda \) has been introduced;

\[
\lambda = \frac{L_0}{T^2}.
\]

The differential equation for the temperature takes the form

\[
\rho c \dot{T} = \lambda \Delta T + \frac{\rho \gamma}{T^3} \Delta \dot{T}.
\]

It is the very same as in equation (22) and also leads to equation (23) with the proper units of length and time. It shows that to make distinction between the above two models may hardly be done experimentally. The first model did not introduce dynamic variables while the other kept the classical formula for the entropy current.

The emerging question is hard to formulate but the above train of thoughts shows clearly that the last word with respect to the entropy flow has not been said.

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REFERENCES


Ván P., On the phenomenological thermodynamics Proceedings of the ICPS'90, Amsterdarn.


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