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MACROSCOPIC INTRODUCTION OF ENTROPY WITH RELAXED ASSUMPTIONS ABOUT REALIZABLE PROCESSES

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State spaces in which not any two states may be connected by a reversible process are possible in models of continuous media with complicated properties. States form which it is generally not possible (within limits of certain models) to return to the initial state, i. e. to realize a cyclic process, are also possible. Some hardening plastic materials whose load bearing surface cannot generally return to its initial shape and position provide examples of models in which parameters of state that define the load bearing surface cannot return to their initial values. Another example is provided by models of hereditary media whose state is determined by the whole history of the strain tensor.

When any two states can be connected by a process (which shows the feasibility of closed processes) the macroscopic formulation of the Second Law of thermodynamics for processes involving homogeneous materials is of the form [1]

$$\int \frac{Q^{\cdot e}}{T}\, dt \leqslant 0 \tag{1}$$

and in the case of nonhomogeneous materials it is of the form

$$\int dt \int\limits_{V} \left(\rho \frac{q^{\cdot}}{T} - \operatorname{div} \frac{\mathbf{q}}{T}\right) dV \leqslant 0 \tag{2}$$

where integration with respect to time t is carried out during the course of any process that begins and ends in the same state; $Q^{\cdot e}$ is the rate of heat flow to a body, $q^{\cdot}$ is the density of the bulk heat intake rate, $\mathbf{q}$ is the heat flux vector, T is the absolute temperature, ρ is the body density, and V denotes the region occupied by the body. If any two states can be linked by reversible processes, such processes can be used for defining entropy and for proving that formula (1) is equivalent to the statement [1]; there exists a function of state S (called entropy) such that in any process

$$dS = d_e S + d_i S, \quad d_e S = dQ^{e}/T, \quad d_i S \geqslant 0$$

The respective reasoning is not directly applicable in the absence of reversible processes, and in the case when not any two states can be linked by a process it is necessary to alter formulations (1) and (2) themselves.

First of all we replace (1) and (2) by a formulation that is equivalent to them on the usual assumptions about realizable processes, but without mentioning cyclic processes.

For brevity we denote the process that begins at instant t_1 in state A and finishes at instant t_2 in state B by π_{AB} and a cyclic process by π_{AA}. We denote by

$J(\pi_{AB})$ the quantity

$$\int_{t_1}^{t_2} dt \int_V \left(\rho \frac{q^{\cdot}}{T} - \operatorname{div}\frac{\mathbf{q}}{T}\right) dV$$

where all quantities relate to process π_{AB} . Process π_{AC} which consists of carrying out consecutively processes π_{AB} and π_{BC} is denoted by $\pi_{AB}\pi_{BC}$.

In this notation formulas (1) and (2) assume for any π_{AA} the form

$$J(\pi_{AA}) \leqslant 0 \tag{3}$$

If any two states can be linked by a process, formula (3) is equivalent to the condition: for any two states A and B

$$\sup_{\pi_{AB}} J(\pi_{AB}) < +\infty \tag{4}$$

(the upper bound is taken over all processes π_{AB}).

Indeed, since (3) implies that

$$J(\pi_{AB}\pi'_{BA}) = J(\pi_{AB}) + J(\pi'_{BA}) \leqslant 0$$

hence for fixed π'_{BA} we have (4). Conversely (3) follows from (4), since in the presence of process π'_{AA} with $J(\pi'_{AA}) = \alpha > 0$ we would have

$$\sup_{\pi_{AA}} J(\pi_{AA}) = +\infty$$

(it is sufficient to consider a multiple repetition of process π'_{AA}).

The quantitative macroscopic formulation by (4) of the Second Law of thermodynamics is also applicable to models within whose limits not any two states can be linked by a process. The fulfilment of inequality (4) may be considered as the necessary condition for the possibility of extending this model to processes linking any two states, and to have the Second Law of thermodynamics in conventional formulation (1) and (2). Such extension of the model should always be possible; for example, in the case of models of solid bodies that are plastically deformable or bodies that have hereditary properties it is sufficient to take fusion into consideration.

Below we apply the relaxed assumption about realizable processes: there exists in the space of states a space * such that process π_{*P} is realizable for any state P. Condition (4) is then equivalent to the statement: there exists an entropy, a function of state S , such that for any process π_{AB}

$$S(B) - S(A) \geqslant J(\pi_{AB}) \tag{5}$$

Formula (4) obviously follows from (5). Conversely, if we set

$$S(P) = S_*(P) = \sup_{\pi_{*P}} J(\pi_{*P})$$

then for the process $\pi_{*B} = \pi_{*A}\pi_{AB}$

$$S_*(B) \geqslant J(\pi_{*B}) = J(\pi_{*A}) + J(\pi_{AB})$$

for any π_{*A} . Hence (5) is satisfied.

Expressions other than S_* are generally also possible for entropy S.

An example of arbitrariness of entropy selection. Let for a thermoelastic-plastic body the density of internal energy U and stresses p^{ij} be defined, as in the corresponding elastic model, by the elastic strain $\varepsilon_{ij}{}^{e}$ and temperature T

$$U = U_e(\varepsilon_{ij}{}^{e}, T), \quad p^{ij} = p_e{}^{ij}(\varepsilon_{ij}{}^{e}, T)$$

with the body load carrying surface defined by the Mises equation

$$f = {}^1\!/_2\, p'^{ij} p_{ij}' - k^2(T, \chi) = 0 \quad (p_{ij}' = p_{ij} - {}^1\!/_3\, p_k{}^k g_{ij})$$

and let the determining relations for plastic strains $\varepsilon_{ij}{}^{p}$ and for the parameter χ of hardening be of the form

$$\chi^{\cdot} = p^{ij} \varepsilon_{ij}^{\cdot p}, \quad \varepsilon_{ij}^{\cdot p} = \begin{cases} h \dfrac{\partial f}{\partial p^{ij}} f^{\cdot} & \text{if} \quad f = 0,\ f^{\cdot} > 0 \\ 0 \end{cases}$$

while in the opposite case

$$\left(f^{\cdot} = \frac{\partial f}{\partial p^{ij}} p^{\cdot ij} + \frac{\partial f}{\partial T} T^{\cdot}\right)$$

On the usual assumptions about $\mathbf{q}$ and that the bulk density of entropy s depends on the parameters of state $\varepsilon_{ij}{}^{e}$, T, and χ inequality (5) for entropy

$$Ts^{\cdot} \geqslant \frac{q^{\cdot}}{T} - \frac{1}{\rho} \operatorname{div} \frac{\mathbf{q}}{T}$$

is equivalent to conditions

$$\frac{\partial U}{\partial \varepsilon_{ij}{}^{e}} - \frac{1}{\rho} p^{ij} - T \frac{\partial s}{\partial \varepsilon_{ij}{}^{e}} = 0, \quad \frac{\partial U}{\partial T} - T \frac{\partial s}{\partial T} = 0 \tag{6}$$

$$\left(\frac{1}{\rho} p^{ij} + T \frac{\partial s}{\partial \chi} p^{ij}\right) \varepsilon_{ij}^{\cdot p} \geqslant 0$$

To satisfy (6) it is sufficient to take for s the entropy density of the corresponding elastic model $s = s_e(\varepsilon_{ij}{}^{e}, T)$. In addition it is also possible to use any function

$$s = s_e(\varepsilon_{ij}{}^{e}, T) + s_1(\chi), \quad \frac{ds_1}{d\chi} \geqslant 0$$

In fact conditions (6) are, as previously, satisfied (the last of these in satisfied owing to the inequality $p^{ij}\varepsilon_{ij}{}^{\cdot p} \geqslant 0$ which follows from the determining relations).

This example shows that for models with complicated properties the entropy can be defined with considerable arbitrariness, and not only to the additive constant.

For the uniqueness of entropy (accurate to the additive constant) it is sufficient that for any state P the sequencies of processes $\{\pi_{*P}^{(n)}\}$ and $\{\pi_{P*}^{(n)}\}$ such that

$$\lim_{n\to\infty} J(\pi_{*P}^{(n)}) + \lim_{n\to\infty} J(\pi_{P*}^{(n)}) = 0 \tag{7}$$

be realizable, since then by virtue of (5)

$$\lim_{n\to\infty} J(\pi_{*P}^{(n)}) \leqslant S(P) - S(*) \leqslant -\lim_{n\to\infty} J(\pi_{P*}^{(n)}) = \lim_{n\to\infty} J(\pi_{*P}^{(n)})$$

$$S(P) = S(*) + \lim_{n\to\infty} J(\pi_{*P}^{(n)})$$

where the limit is independent of the selection of sequence of $\{\pi_{*P}^{(n)}\}$ in (7).

Condition (7) is satisfied in many models of continuous media by sequencies obtained by slowing down some processes π_{*P} and π_{P*} which are usually replaced by "infinitely slow reversible processes".

The considered here scheme for the definition of entropy is applicable also in the case of some other assumptions about realizable processes. For instance, it is possible on the assumption of feasibility of processes π_{P*} (but not π_{*P}) to set

$$S(P) = S^*(P) = -\sup_{\pi_{P*}} J(\pi_{P*})$$

It is also possible to consider instead of π_{*P} processes that are in some sense approximations of the state P. In particular, the entropy for media with fading memory [2] may be determined in this manner without using the assumption about the behavior of medium in a slowed down process.

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REFERENCES

1. Sedov, L. I., Mechanics of Continuous Medium, Vol. 1. Moscow, "Nauka", 1973. (see also English Translation, Pergamon Press, Book No. 09878, 1965).

2. Day, W. A., Thermodynamics of Simple Media with Memory. Moscow, "Mir", 1974.

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