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SUBSTANTIAL BALANCE EQUATION OF INTERNAL ENERGY AS VIEWED BY THE BALANCE THEORY

Z. Wrzesiński

Warsaw University of Technology,
Plac Politechniki 1,
00-661 Warsaw, Poland

The article defines the microscopic substantial system and elementary first-order increments of elementary third-order increments of internal energy (IE), friction heat and heat exchanged between the substantial microsystem and the exterior. A substantial balance of internal energy (IE) has been presented for extensive quantities (EQ) with reference to a substantial microsystem which has been next transformed into a substantial balance equation of the mass density of internal energy (IE). The substantial balance equation of the mass density of internal energy has been integrated for a substantial system throughout the whole substantial area, obtaining a substantial balance equation of internal energy for intensive quantities related to this area. It has also been defined under what conditions this balance equation can be used in the substantial area. In the case of the reversible change, the substantial balance equation of internal energy (IE) for intensive quantities has been reduced to the equation commonly called the first principle of thermodynamics for intensive quantities.

Due to the fact that the substance is where internal energy (IE) is placed (in contrast to, e.g. the energy of a magnetic field), its basic balance will be considered in a substantial area, each point of which moves in the same way as the substance, i.e. at substantial velocity $\overline{u}$ (of the local and instantaneous mass centre). Substantial elements of geometrical volume, surface, lines will be distinguished by an arrow symbol $\to \overline{u}$ placed below the proper letter.

In an arbitrary place of macroscopic substantial system $\underset{\to\overline{u}}{V}$ we will differentiate an elementary third-order increment of the volume $\underset{\longrightarrow\overline{u}}{d^3V}$ constituting a microscopic substantial system presented in the figure given below.

According to Fig. 1, an elementary third-order increment of the $\underset{\longrightarrow\overline{u}}{d^2\overline{A}}$ volume of a substantial micro-system equals the scalar product of $\underset{\longrightarrow\overline{u}}{d\overline{x}}$ elementary second-order increment vectors of the substantial surface and an elementary first-order increment of the displacement vector of the substantial surface

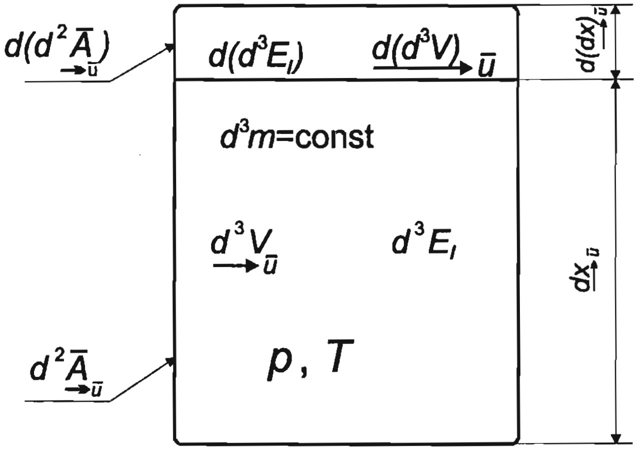

FIG. 1. Microscopic substantial system.

(1) $$d^3V_{\longrightarrow\overline{u}} = \left(d^2\overline{A}_{\longrightarrow\overline{u}} \cdot d\overline{x}_{\longrightarrow\overline{u}} \right).$$

However, the elementary first-order increment of an elementary third-order increment of the substantial micro-system volume is equal to

(2) $$d(d^3V)_{\longrightarrow\overline{u}} = \left(d(d^2\overline{A}_{\longrightarrow\overline{u}}) \cdot d\overline{x}_{\longrightarrow\overline{u}} \right).$$

The elementary third-order increment of mass d^3m filling an elementary third-order increment of volume $d^3V_{\longrightarrow\overline{u}}$ of the substantial micro-system is, by definition of a substantial system, constant and expressed by the following relation:

(3) $$d^3m = \rho \; d^3V_{\longrightarrow\overline{u}} = \text{const}$$

where ρ stands for the volume density of mass.

The mass density of heat quantity q for the substantial micro-system $d^3V_{\longrightarrow\overline{u}}$ is defined as the quotient of an elementary third-order heat increment d^3Q exchanged between the micro-system and the exterior, and an elementary third-order mass increment d^3m contained in the substantial system

(4) $$q = \frac{d^3Q}{d^3m}.$$

The mass density of heat friction q_f for the substantial micro-system will be expressed by the following relation:

(5) $$q_f = \frac{d^3Q_f}{d^3m},$$

where d^3Q_f stands for an elementary third-order friction heat increment created in substantial micro-system $d^3V_{\longrightarrow\overline{u}}$. The elementary first-order increments mass density of heat δq and friction δq_f for the substantial micro-system are expressed respectively by the relations

$$\delta q = \delta\left(\frac{d^3Q}{d^3m}\right) = \frac{\delta(d^3Q)}{d^3m} \tag{6}$$

and

$$\delta q_f = \delta\left(\frac{d^3Q_f}{d^3m}\right) = \frac{\delta(d^3Q_f)}{d^3m}\,. \tag{7}$$

Moving from substantial micro-system $d^3V_{\longrightarrow\overline{u}}$ to substantial macrosystem $V_{\to\overline{u}}$ we will separate the variables in relation (6) and integrate them within the limits

$$\delta q \iiint\limits_0^m d^3m = \delta \iiint\limits_0^Q d^3Q\,. \tag{8}$$

After the integration we will obtain the relation defining the elementary first-order mass-density increment of heat for a substantial macro-system.

$$\delta q = \frac{\delta Q}{m}\,. \tag{9}$$

Using the same algorithm with reference to equation (7), we will obtain a relation defining the elementary first-degree mass-density increment of friction heat for a substantial macro-system

$$\delta q_f = \frac{\delta Q_f}{m}\,. \tag{10}$$

The mass-density of internal energy for a substantial micro-system is expressed by the following relation:

$$\varepsilon_I = \frac{d^3E_I}{d^3m}\,, \tag{11}$$

thus the elementary first-order mass-density increment of internal energy is defined by the relation.

$$d\varepsilon_I = d\left(\frac{d^3E_I}{d^3m}\right) = \frac{d(d^3E_I)}{d^3m}\,. \tag{12}$$

Obviously, the mass-density of volume ϑ (specific volume) and volume-density of mass ρ, according to their definitions, are expressed respectively by the relations

$$\underset{\to\overline{u}}{\vartheta} = \frac{d^3\underset{\longrightarrow\overline{u}}{V}}{d^3m}\,, \tag{13}$$

$$\rho = \frac{d^3m}{d^3\underset{\longrightarrow\overline{u}}{V}}\,. \tag{14}$$

Because internal energy is an extensive quantity, the change of IE storage contained in the substantial system, as in the case of every extensive quantity, consists of an exchange with the exterior through the system boundaries (inflow, outflow) and of production (creation, annihilation) within the system. Consequently, the balance of internal energy is expressed, according to the principles of non-equilibrium thermodynamics, by the relation

$$\underbrace{\underbrace{d\underset{\longrightarrow\overline{u}}{E_I}}_{change} = \underbrace{\delta Q_f + \sum_{\alpha=1}^{\gamma+1}\left(\overline{F}_\alpha\cdot d\overline{X}_\alpha\right) - p\,d\underset{\longrightarrow\overline{u}}{V}}_{production} + \underbrace{\delta Q}_{exchange}}_{of\ IE\ storage\ in\ the\ substantial\ system}\,. \tag{15}$$

In the above balance, the sum of products of generalised forces and elementary generalised displacements takes account of electromagnetic phenomena ignored in classical thermodynamics. The balance of internal energy for substantial micro-system $d^3\underset{\longrightarrow\overline{u}}{V}$ is expressed in the same way as in the case of substantial system $\underset{\to\overline{u}}{V}$, the only difference appearing in the scale of balancing areas.

Thus we can write as follows:

$$\underbrace{\underbrace{d(d^3E_I)_{\longrightarrow\overline{u}}}_{change} = \underbrace{\delta(d^3Q_f) + \sum_{\alpha=1}^{\gamma+1}(\overline{F}_\alpha\cdot d(d^3\overline{X}_\alpha) - pd(d^3\underset{\to\overline{u}}{V})}_{production} + \underbrace{\delta(d^3Q))}_{exchange}}_{of\ IE\ storage\ in\ the\ substantial\ micro-system}\,. \tag{16}$$

Considering relations (6), (7), (12) and (0.14), we can write that:

- the elementary first-order increment of the third-order IE increment of the substantial micro-system equals

$$d(d^3E_I) = d\varepsilon_I\rho\, d^3\underset{\longrightarrow\overline{u}}{V}\,; \tag{17}$$

- the elementary first-order increment of the elementary third-order increment of friction heat exchanged between the substantial micro-system and the exterior equals

(18) $$\delta(d^3Q) = \delta q\, \rho\, \underset{\longrightarrow \overline{u}}{d^3V}\ ;$$

- the elementary first-order of the elementary third-order increment of friction heat created in the substantial micro-system equals

(19) $$\delta(d^3Q_f) = \delta q_f\, \rho\, \underset{\longrightarrow \overline{u}}{d^3V}\ .$$

Taking account of the above assumption that generalised forces appearing in the effective work segment of the substantial balance of internal energy are conjugated with their corresponding generalised displacements in such a way that their products form elementary first-order increments of third-order effective work increments, we can write as follows:

(20) $$d(d^3L_u) = \sum_{\alpha=1}^{\gamma} (\overline{F}_\alpha \cdot d(d^3\overline{X}_\alpha)).$$

Substituting (0.17), (0.18), (0.19) and (20) into (0.16), we obtain

(21) $$\underset{\longrightarrow \overline{u}}{d\varepsilon_L}\, \rho\, \underset{\longrightarrow \overline{u}}{d^3V} = \delta q_f\, \rho\, \underset{\longrightarrow \overline{u}}{d^3V} + \sum_{\alpha=1}^{\gamma+1} \left(\overline{F}_\alpha \cdot d(d^3\overline{X}_\alpha) - pd\,(\underset{\longrightarrow \overline{u}}{d^3V}) + \delta q\, \rho\, \underset{\longrightarrow \overline{u}}{d^3V} \right).$$

Dividing the last equation by the elementary third-order increment of mass d^3m contained in the area of a substantial micro-system, we will obtain

(22) $$\underset{\longrightarrow \overline{u}}{d^3\varepsilon_I}\, \rho\, \frac{\underset{\longrightarrow \overline{u}}{d^3V}}{d^3m} = \delta q_f\, \rho\, \frac{\underset{\longrightarrow \overline{u}}{d^3V}}{d^3m} + \sum_{\alpha=1}^{\gamma+1} \left(\overline{F}_\alpha \cdot \frac{d(d^3\overline{X}_\alpha)}{d^3m} \right) - pd\left(\frac{\underset{\longrightarrow \overline{u}}{d^3V}}{d^3m} \right) + \delta q\, \rho\, \frac{\underset{\longrightarrow \overline{u}}{d^3V}}{d^3m}\ .$$

Taking account of the definition of mass-density of volume (relation (0.13)) in the above equation as well as the constant character of mass $d^3m = \text{const}$ contained in the elementary third-order increment of volume $\underset{\longrightarrow \overline{u}}{d^3V}$ of the substantial micro-system, and also defining the mass generalised coordinate as the ratio of the elementary third-order increment of generalised coordinate $d^3\overline{X}_\alpha$ to the elementary third-order of mass increment of d^3m,

(23) $$\overline{x}_\alpha = \frac{d^3\overline{X}_\alpha}{d^3m}\ ,$$

we will obtain a substantial balance equation of the mass-density of internal energy for substantial micro-system $\underset{\longrightarrow\overline{u}}{d^3V}$ expressed by the relation below

$$(24)\qquad \underbrace{\underbrace{\underset{\longrightarrow\overline{u}}{d\varepsilon_I}}_{change} = \underbrace{\delta Q_f + \sum_{\alpha=1}^{\gamma+1}\left(\overline{F}_\alpha\cdot d\overline{x}_\alpha\right) - p\,\underset{\longrightarrow\overline{u}}{d\vartheta}}_{production} + \underbrace{\delta q}_{exchange}}_{of\ IE\ mass\ density\ at\ the\ substantia\ 1\ point} .$$

Multiplying the last relationship by volume density of mass and dividing by an elementary time increment, we will obtain the balance of internal energy (IE) at the substance point

$$(25)\qquad \underbrace{\underbrace{\rho\frac{\underset{\longrightarrow\overline{u}}{d\varepsilon_I}}{dt}}_{change\ velocity} = \underbrace{\rho\frac{dq_f}{dt} + \sum_{\alpha=1}^{\gamma+1}\rho\left(\overline{F}_\alpha\cdot\frac{d\overline{x}_\alpha}{dt}\right) - \rho p\frac{\underset{\longrightarrow\overline{u}}{d\varepsilon}}{dt}}_{production\ velocity} + \underbrace{\rho\frac{dq}{dt}}_{exchange\ velocity}}_{of\ IE\ mass\ density\ at\ the\ substantia\ 1\ point} .$$

According to [1], the right-hand side of the above balance of internal energy (IE) at the substantial point or otherwise, production velocity and exchange velocity of IE volume density consists of the following parts which respectively describe:

$$\rho\frac{dq_f}{dt} = -\left(\overline{\overline{\Pi}}_V : \overline{\overline{\operatorname{grad}\overline{u}}}\right) > 0$$

- irreversible creation of thermal energy at the expense of kinetic energy (viscous dissipation)

$$\rho\left(\overline{F}_1\cdot\frac{d\overline{x}_1}{dt}\right) = -\left(\underset{\to\overline{u}}{\overline{K}}\cdot\underset{\to\overline{u}}{\overline{i}}\right) \gtrless 0\,;$$

- reversible conversion of binding energy (electrochemical phenomena) or thermal energy (thermoelectric phenomena) with electromagnetic energy

$$\rho\left(\overline{F}_2\cdot\frac{d\overline{x}_2}{dt}\right) = -\left(\kappa\,\underset{\to\overline{u}}{\overline{i}}\cdot\underset{\to\overline{u}}{\overline{i}}\right) > 0\,;$$

- irreversible creation of thermal energy at the expense of electromagnetic energy (Joule's heat during electric conduction)

$$\rho\left(\overline{F}_3\cdot\frac{d\overline{x}_3}{dt}\right) = G_{pm} > 0\,;$$

- irreversible creation of thermal energy at the expense of electromagnetic energy (heat of polarising-magnetic hysteresis)

$$\rho p \,\frac{d\vartheta}{\underset{\to\overline{u}}{} dt} = \left(\overline{\overline{\Pi}}_p : \overline{\overline{\operatorname{grad}\overline{u}}}\right) \gtrless 0\,;$$

- reversible conversion of thermal energy with kinetic energy in a liquid (compression, expansion)

$$\rho\frac{dq}{dt} = -\operatorname{div}\overline{J}_{nc} > 0\,;$$

- non-convective exchange stream of internal energy by way of diffusion, conduction and radiation

In these formulas:

$\overline{\overline{\Pi}}_V$ – stands for viscous stress in the liquid,

$\underset{\to\overline{u}}{K}$ – motive vector (taking account of electric micro-field properties – forces of the electrochemical and thermoelectric nature),

$\underset{\to\overline{u}}{i}$ – vector of current density,

κ – resistivity,

G_{pm} – density of polarising-magnetic conversion – it accompanies polarisation and magnetic hysteresis,

$\overline{\overline{\Pi}}_p$ – pressure stress,

$\overline{J}_{nc}$ – non-convective transfer-stream density of internal energy by diffusion, conduction and radiation.

We will obtain a substantial balance equation of internal energy mass-density for substantial macro-system $\underset{\to\overline{u}}{V}$ by transforming equation (0.21) into the form presented below (0.26).

In classical thermodynamics, which assumes quasi-static states, all fields are treated as non-gradient within the area under consideration.

$$\text{(26)}\qquad \underset{\longrightarrow\overline{u}}{d\varepsilon}\,\rho\, d^3\underset{\longrightarrow\overline{u}}{V} = \delta q_f\,\rho\, d^3\underset{\longrightarrow\overline{u}}{V} + \sum_{\alpha=1}^{\gamma+1}(\overline{F}_\alpha\cdot d^3(d\overline{X}_\alpha))$$

$$- pd^3(d\underset{\longrightarrow\overline{u}}{V}) + \delta q\cdot\rho\cdot d^3\underset{\longrightarrow\overline{u}}{V}\ .$$

We will integrate the above equation within the limits:

$$(27)\quad d\varepsilon_I \iiint\limits_0^{\underset{\to\overline{u}}{V}} \rho\, d^3\underset{\longrightarrow\overline{u}}{V} = \delta q_f \iiint\limits_0^{\underset{\to\overline{u}}{V}} \rho\, d^3\underset{\longrightarrow\overline{u}}{V} + \sum_{\alpha=1}^{\gamma+1}\left(\iiint\limits_0^{dX_\alpha} (\overline{F}_\alpha \cdot d^3(d\overline{X}_\alpha))\right)$$

$$- \iiint\limits_0^{\underset{\longrightarrow\overline{u}}{dV}} p d^3\left(d\underset{\longrightarrow\overline{u}}{V}\right) + \delta q \iiint\limits_0^{\underset{\to\overline{u}}{V}} \rho d^3 \underset{\longrightarrow\overline{u}}{V}\,.$$

The integrals of equation (0.27) are calculated in the following way; the first one – by taking account of the definition of the volume density of mass

$$(28)\qquad \iiint\limits_0^{\underset{\to\overline{u}}{V}} \rho d^3\underset{\longrightarrow\overline{u}}{V} = \iiint\limits_0^{\underset{\to\overline{u}}{V}} \frac{d^3 m}{d^3\underset{\longrightarrow\overline{u}}{V}} \cdot d^3\underset{\longrightarrow\overline{u}}{V} = \iiint\limits_0^{m} d^3 m = m\,.$$

The second and third integrals are obtained by assuming that the field of pressure p in the elementary first-order volume increment of substantial area is non-gradient (homogenous)

$$(29)\qquad \overline{\operatorname{grad}}\, p = \overline{0}\,,$$

and by assuming that the field of generalised forces $\overline{F}_\alpha$ is non-gradient (homogenous) on elementary first-order of displacement increment $d\overline{X}_\alpha$

$$(30)\qquad \overline{\overline{\operatorname{grad}}}\, \overline{F}_\alpha = \overline{\overline{0}}\,.$$

Thus we can write that elementary thermodynamic work is defined by the following relation:

$$(31)\qquad \iiint\limits_0^{\underset{\to\overline{u}}{dV}} p d^3\,(d\underset{\longrightarrow\overline{u}}{V}) = \iiint\limits_0^{\underset{\longrightarrow\overline{u}}{dV}} (d\underset{\longrightarrow\overline{u}}{V}) = p\, d\underset{\longrightarrow\overline{u}}{V}$$

but the elementary work of generalised forces on an elementary generalised displacement increment is defined by the relation

$$(32)\qquad \iiint\limits_0^{d\overline{X}_\alpha} (\overline{F}_\alpha \cdot d^3(d\overline{X}_\alpha)) = \left(\overline{F}_\alpha \cdot \iiint\limits_0^{d\overline{X}_\alpha} d^3(d\overline{X}_\alpha)\right) = (\overline{F}_\alpha \cdot d\overline{X}_\alpha)\,.$$

We will separate the coordinates in expression (23) defining generalised coordinate $\overline{X}_\alpha$, and next we will integrate this expression

$$\iiint_0^{\overline{x}_\alpha} d^3\overline{X}_\alpha \equiv \iiint_0^{m} \overline{x}_\alpha d^3 m \,. \tag{33}$$

If we assume that generalised mass coordinate $\overline{x}_\alpha$ is non-gradient in a substantial micro-area containing an elementary third-order mass increment

$$\overline{\overline{\text{grad}}}\,\overline{x} = \overline{\overline{0}}\,, \tag{34}$$

then the integral on the right-hand side of Eq. (0.33) will define the value of a generalised coordinate

$$\overline{X}_\alpha = \overline{x}_\alpha \cdot m \,. \tag{35}$$

Thus the generalised mass coordinate, with condition (34) taken into account, will be expressed by the following relationship:

$$\overline{x}_\alpha = \frac{\overline{X}_\alpha}{m} \,. \tag{36}$$

By applying the same procedure in relation to Eq. (0.13) defining mass-density of volume, we will obtain

$$\iiint_0^{m} \underset{\to\overline{u}}{\vartheta} d^3 m = \iiint_0^{\underset{\to\overline{u}}{V}} d^3 \underset{\longrightarrow\overline{u}}{V} \,. \tag{37}$$

Assuming that the field of the mass-density of volume (specific volume) is non-gradient (homogenous)

$$\overline{grad}\,\vartheta = \overline{0}\,, \tag{38}$$

we will calculate the value of the integral defined by equation (0.37),

$$\underset{\to\overline{u}}{\vartheta} \cdot m = \underset{\to\overline{u}}{V} \tag{39}$$

and hence we will determine the relation describing the mass-density of volume (with condition (38) satisfied)

$$\underset{\to\overline{u}}{\vartheta} = \frac{\underset{\to\overline{u}}{V}}{m} \,. \tag{40}$$

Taking account of the assumptions made about the homogeneity of pressure fields (0.29) of mass-densities of volume (38) inside a substantial system and about the homogeneity of the fields of generalised forces (0.30) as well as the assumption about non-gradient generalised coordinate (0.34) and also taking account of the integration results of (0.28), (0.31), (32) in Eq. (0.27), we will obtain

$$d\varepsilon_I \cdot m = \delta q_f \cdot m + \sum_{\alpha=1}^{\gamma+1} (\overline{F}_\alpha \cdot d\overline{X}_\alpha) - p \, \underset{\longrightarrow \overline{u}}{dV} + \delta q \cdot m \,. \tag{41}$$

Taking into account the above assumptions and the fact that mass storage is constant in substantial system $\underset{\rightarrow \overline{u}}{V}$

$$m = \mathrm{const}\,, \tag{42}$$

after dividing Eq. (0.41) by mass and taking into account relations (34) and (0.40), we will obtain a substantial balance equation of internal energy for intensive quantities (IQs).

$$\underbrace{\underbrace{\underset{\longrightarrow \overline{u}}{d\varepsilon_I}}_{\textit{change}} = \underbrace{\delta q_f + \sum_{\alpha=1}^{\gamma+1} \left(\overline{F}_\alpha \cdot d\overline{x}_\alpha\right) - p \, \underset{\longrightarrow \overline{u}}{d\vartheta}}_{\textit{production}} + \underbrace{\delta q}_{\textit{exchange}} \;.}_{\textit{of IE mass density}} \tag{43}$$

From a formal point of view concerning the transcription of substantial balance equations, the mass density of internal energy for substantial micro-system $\underset{\longrightarrow \overline{u}}{d^3V}$ expressed by Eq. (0.24), and from the point of substantial macro-system $\underset{\rightarrow \overline{u}}{V}$ expressed by Eq. (0.43), there is no difference between the two. However, in formulating the substantial balance equation of internal energy mass-density for substantial system (0.43), assumptions were made about the homogeneity of pressure fields, mass densities of volume, generalised coordinates and generalised forces, which made it possible to integrate the initial Eq. (0.26) concerning the substantial micro-system and to obtain the substantial balance equation of internal energy mass-density for substantial system $\underset{\rightarrow \overline{u}}{V}$.

If the substantial $\underset{\rightarrow \overline{u}}{V}$ system $\underset{\rightarrow \overline{u}}{V}$ is not affected by the exterior, or when generalised forces fulfil the condition

$$\overline{F}_\alpha = \overline{0} \tag{44}$$

for $\alpha = 1, 2, ..., \gamma$, then the substantial balance equation of internal energy for (IQs) will be as follows:

$$\underbrace{\underbrace{\underset{\longrightarrow \overline{u}}{d\varepsilon_{I}}}_{\textit{change}} = \underbrace{\delta q_{f} - p\, d\vartheta}_{\textit{production}} + \underbrace{\delta q}_{\textit{exchange}}}_{\textit{of IE mass density}} . \tag{45}$$

The substantial balance equation of internal energy (IE) for intensive quantities (IQs) expressed by equation (0.43) is the basis on which we can formulate the first principle of thermodynamics for intensive quantities (IQs). The first principle of thermodynamics for IQs is a substantial balance equation of internal energy for IQs referring to the conditions of a reversible thermodynamic process, or referring to a thermodynamic process which goes on under the conditions of thermodynamic equilibrium without any friction

$$\delta q_{f} = 0 . \tag{46}$$

Considering the above statement and the constraint defined by relation (46), we can write an equation describing, in its most developed form, the first principle of thermodynamics for intensive quantities (IQs).

$$\underbrace{\underbrace{\underset{\longrightarrow \overline{u}}{d\varepsilon_{I}}}_{\textit{change}} = \underbrace{\sum_{\alpha=1}^{\gamma+1} (\overline{F}_{\alpha} \cdot d\overline{x}_{\alpha}) - p\, d\vartheta}_{\textit{production}} + \underbrace{\delta q}_{\textit{exchange}}}_{\textit{of IE mass density}} . \tag{47}$$

On the other hand, if the elementary mass-density increment of external work equals zero

$$\delta l_{z} = 0 , \tag{48}$$

which means the exterior does not affect the system, then the first principle of thermodynamics for intensive quantities (IQs) will take the form expressed by the following equation:

$$\underbrace{\underbrace{\underset{\longrightarrow \overline{u}}{d\varepsilon_{I}}}_{\textit{change}} = \underbrace{- p\, d\vartheta}_{\textit{production}} + \underbrace{\delta q}_{\textit{exchange}}}_{\textit{of IE mass density}} . \tag{49}$$

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