Towards a Fundamental Structure of Continuum Mechanics

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For a class of systems obeying Euler's equation of motion the existence of a quantity to be named "proper mechanical energy" (PME) is shown which, together with internal energy, results in a quantity to be named "proper energy" (PE), which is conserved under conditions of time-dependent potentials. The appertaining formal structure for the continuum mechanics of such systems is the counterpart to Gibbs' fundamental equation of thermodynamics and the relations deriving therefrom. Euler's equation of motion, in particular, corresponds to the Gibbs-Duhem equation of thermodynamics. The transport properties of PME and PE are different from those of the corresponding conventional energies. The results point to a general structure of this kind for continuum mechanics.

I. Introduction

Basic to the conventional treatment of continuum mechanics is the balance of momentum being equivalent to the equation of motion. The topic of this paper is to show the existence of a deeper structure which corresponds to the structure of thermodynamics. This is done first for a barotropic system. Then the discussion is extended to more general systems. Necessary is the existence of potentials for acceleration and forces. For general continuum mechanics tensorial potentials have to be introduced (will be discussed in a following paper).

Section II recapitulates the customary balance equations of continuum mechanics. In Sect. III the new concept is developed for barotropic systems. In Sect. IV, the transport properties of the quantities introduced in Sect. III are discussed. Section V shows the relation to Bernoulli's equation. In Sect. VI, the approximation incompressibility is considered and a simple example is presented to demonstrate the peculiar properties of what is called proper mechanical energy. The seventh extends the discussion to a class of irreversible systems. In Sect. VIII a structurally essential correction is introduced. In Sect. IX the irreversible systems are discussed from the corrected point of view. Finally the new structure is applied to blackbody radiation.

II. Balance of Mechanical Energy in its Customary Form

For every extensive physical quantity Y of a continuous system there exists a spatial balance equation

$$\frac{\partial y}{\partial t} = - \operatorname{div} \boldsymbol{y} + \pi_Y \tag{1}$$

with $\partial/\partial t$ the spatial time derivative; y the density, $\boldsymbol{y}$ the flux vector, π_Y the source term of the quantity Y.

Using the relation between spatial and material time derivative

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \boldsymbol{v} \cdot \operatorname{grad} \tag{2}$$

(d/dt material derivative, $\boldsymbol{v}$ velocity of a material point), (1) can be transformed to

$$\frac{\mathrm{d}y}{\mathrm{d}t} = - y \operatorname{div} \boldsymbol{v} - \operatorname{div}(\boldsymbol{y} - y\boldsymbol{v}) + \pi_Y . \tag{3}$$

$y\boldsymbol{v}$ is the convective part of the flux. If $\boldsymbol{y}$ is purely convective, the second member of the right-hand side vanishes. The proper choice of source-term and flux in (1) or (3) is a matter of physical consistency.

To get the balance equation for the mechanical energy of a fluid without shear viscosity, Euler's equation of motion

$$m \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} + \operatorname{grad} P + m \operatorname{grad} \varphi = 0 \tag{4}$$

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is multiplied scalarly by $\boldsymbol{v}$ (m mass density, P pressure, φ potential of the force field; in this paper, only gravitational forces will be considered; their potential may, however, be time-dependent). Transformation of the different terms yields

$$m\,\boldsymbol{v}\cdot\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}=\frac{\mathrm{d}m\,\boldsymbol{v}^2/2}{\mathrm{d}t}+\frac{m\,\boldsymbol{v}^2}{2}\operatorname{div}\boldsymbol{v}\,,$$

where the continuity equation for mass

$$\frac{\mathrm{d}m}{\mathrm{d}t}=-\,m\operatorname{div}\boldsymbol{v} \tag{5}$$

has been used;

$$\boldsymbol{v}\cdot\operatorname{grad}P=\operatorname{div}P\boldsymbol{v}-P\operatorname{div}\boldsymbol{v};$$

and

$$m\boldsymbol{v}\cdot\operatorname{grad}\varphi=\frac{\mathrm{d}m\,\varphi}{\mathrm{d}t}+m\,\varphi\operatorname{div}\boldsymbol{v}-m\frac{\partial\varphi}{\partial t}\,,$$

where (2) and (5) have been employed.

Then the balance equation for mechanical energy is

$$\frac{\mathrm{d}m\left(\frac{\boldsymbol{v}^2}{2}+\varphi\right)}{\mathrm{d}t}=-\,m\left(\frac{\boldsymbol{v}^2}{2}+\varphi\right)\operatorname{div}\boldsymbol{v}-\operatorname{div}P\boldsymbol{v}+P\operatorname{div}\boldsymbol{v}+m\frac{\partial\varphi}{\partial t} \tag{6}$$

with $m\left(\frac{\boldsymbol{v}^2}{2}+\varphi\right)$ its density and $P\operatorname{div}\boldsymbol{v}+m\frac{\partial\varphi}{\partial t}$ its source term.

The balance equation for the internal energy U (u its density) of a reversible system is

$$\frac{\mathrm{d}u}{\mathrm{d}t}=-\,u\operatorname{div}\boldsymbol{v}-P\operatorname{div}\boldsymbol{v}\,. \tag{7}$$

with the source term $-P\operatorname{div}\boldsymbol{v}$.

Addition of (6) and (7) results in

$$\frac{\mathrm{d}\left\{m\left(\frac{\boldsymbol{v}^2}{2}+\varphi\right)+u\right\}}{\mathrm{d}t}=-\left\{m\left(\frac{\boldsymbol{v}^2}{2}+\varphi\right)+u\right\}\operatorname{div}\boldsymbol{v}-\operatorname{div}P\boldsymbol{v}+m\frac{\partial\varphi}{\partial t} \tag{8}$$

with the energy density $m\left(\frac{\boldsymbol{v}^2}{2}+\varphi\right)+u$ and the source term $m\frac{\partial\varphi}{\partial t}$. For conservation of this energy the condition $\frac{\partial\varphi}{\partial t}=0$ is necessary.

III. A Fundamental Equation for Barotropic Systems

For a barotropic system (i.e. pressure a function of only one variable, conveniently m) $P=P(m)$, and additionally the force field derivable from a potential, which may be time-dependent, there exists an acceleration potential Φ with $\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}=\operatorname{grad}\Phi$ [1]. This is immediately seen if (4) is divided by m and the vector operator curl is applied to it:

$$\operatorname{curl}\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}=-\operatorname{grad}\frac{1}{m}\times\operatorname{grad}P=\frac{1}{m^2}\operatorname{grad}m\times\frac{\partial P}{\partial m}\operatorname{grad}m=0\,. \tag{9}$$

Hence (4) can be written

$$m\operatorname{grad}(\Phi+\varphi)+\operatorname{grad}P=0\,. \tag{10}$$

Equation (10) can be transformed to

$$\operatorname{grad}\{m(\Phi+\varphi)+P\}=(\Phi+\varphi)\operatorname{grad}m\,. \tag{11}$$

Equation (10) scalarly multiplied by $\boldsymbol{v}$, and use of (2) leads to

$$m\frac{\mathrm{d}(\Phi+\varphi)}{\mathrm{d}t}+\frac{\mathrm{d}P}{\mathrm{d}t}=m\frac{\partial(\Phi+\varphi)}{\partial t}+\frac{\partial P}{\partial t}\,. \tag{12}$$

Dividing this equation by m and applying the operation grad to it yields for the right-hand side

$$\operatorname{grad}\left\{\frac{\partial(\Phi+\varphi)}{\partial t}+\frac{1}{m}\frac{\partial P}{\partial t}\right\}=\frac{\partial}{\partial t}\left\{\operatorname{grad}(\Phi+\varphi)+\frac{1}{m}\operatorname{grad}P\right\}+\frac{1}{m^2}\left(\frac{\partial m}{\partial t}\operatorname{grad}P-\frac{\partial P}{\partial t}\operatorname{grad}m\right)=0\,, \tag{13}$$

where the first member on the right-hand side vanishes because of (10), the last member because of $\operatorname{grad}P=\frac{\mathrm{d}P}{\mathrm{d}m}\operatorname{grad}m$. Hence each side of (12) is a function of time only, multiplied by m. The right-hand side of (12) may be written in the form

$$m\frac{\partial(\Phi+\varphi)}{\partial t}+\frac{\partial P}{\partial t}=-\,m\frac{\partial f(t)}{\partial t}\,,$$

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[1] Eulerian dynamics with dependence on locally one thermodynamic variable means reversibility, i.e. local adiabatics and absence of volume viscosity.

where for convenience the time function $\dfrac{\partial f(t)}{\partial t}$ is introduced. This can be transformed to

$$\frac{\partial\{m[\Phi+\varphi+f(t)]+P\}}{\partial t}=[\Phi+\varphi+f(t)]\,\frac{\partial m}{\partial t}\,. \tag{14}$$

Addition of $f(t)$ grad m on both sides of (11) leads to

$$\operatorname{grad}\{m[\Phi+\varphi+f(t)]+P\}=[\Phi+\varphi+f(\mathrm{t})]\operatorname{grad} m\,. \tag{15}$$

The function $f(t)$ in (14) and (15) can be included in the definition of $\Phi+\varphi$. With this convention we introduce

$$a=a(\boldsymbol{r},t)=m(\Phi+\varphi)+P \tag{16}$$

($\boldsymbol{r}$ position) and write (14)

$$\frac{\partial a}{\partial t}=(\Phi+\varphi)\,\frac{\partial m}{\partial t} \tag{17}$$

and (15)

$$\operatorname{grad} a=(\Phi+\varphi)\operatorname{grad} m\,. \tag{18}$$

From $a=a(\boldsymbol{r},t)$ and (17) and (18) follows

$$\begin{aligned}\mathrm{d}a&=\frac{\partial a}{\partial t}\,\mathrm{d}t+\mathrm{d}\boldsymbol{r}\cdot\operatorname{grad} a \qquad\qquad (19)\\ &=(\Phi+\varphi)\left(\frac{\partial m}{\partial t}\,\mathrm{d}t+\mathrm{d}\boldsymbol{r}\cdot\operatorname{grad} m\right)=(\Phi+\varphi)\,\mathrm{d}m\,.\end{aligned}$$

The differential of (16) compared with (19) yields

$$m\,\mathrm{d}(\Phi+\varphi)+\mathrm{d}P=0\,, \tag{20}$$

being integrable because of $P(m)$; i.e. there exists a quantity $a=m(\Phi+\varphi)+P$ with

$$\left(\frac{\partial a}{\partial m}\right)_{\text{barotropic}}=\Phi+\varphi\,. \tag{21}$$

Equation (20) implies the equation of motion (10) and

$$m\,\frac{\partial(\Phi+\varphi)}{\partial t}+\frac{\partial P}{\partial t}=0 \tag{22}$$

and

$$m\,\frac{\mathrm{d}(\Phi+\varphi)}{\mathrm{d}t}+\frac{\mathrm{d}P}{\mathrm{d}t}=0\,. \tag{23}$$

Equation (19) together with (16) and (20) closely corresponds to Gibbs' fundamental equation of thermodynamics. For a one-component system there is

$$\mathrm{d}u=T\,\mathrm{d}s+\mu\,\mathrm{d}n \tag{24}$$

with

$$u=T\,s+\mu\,n-P \tag{25}$$

and

$$s\,\mathrm{d}T+n\,\mathrm{d}\mu-\mathrm{d}P=0 \tag{26}$$

(T absolute temperature, μ chemical potential, s entropy density, n density of mol number).

Barotropy implies $\mathrm{d}s/\mathrm{d}t=-s\operatorname{div}\boldsymbol{v}$. This, together with $\mathrm{d}n/\mathrm{d}t=-n\operatorname{div}\boldsymbol{v}$ by elimination of div $\boldsymbol{v}$ yields $\mathrm{d}\,\dfrac{\ln s/n}{\mathrm{d}t}=0$ and hence $\mathrm{d}\hat{s}/\mathrm{d}t=0$ ($\hat{s}=s/n$ molar entropy). Thus follows $\mathrm{d}s/\mathrm{d}t=\hat{s}\,\mathrm{d}n/\mathrm{d}t$ and therefore

$$\frac{\mathrm{d}u}{\mathrm{d}t}=(T\,\hat{s}+\mu)\,\frac{\mathrm{d}n}{\mathrm{d}t}\quad\text{and}\quad n\,\frac{\mathrm{d}(T\,\hat{s}+\mu)}{\mathrm{d}t}-\frac{\mathrm{d}P}{\mathrm{d}t}=0\,. \tag{27}$$

(For spatial time derivatives and gradients the correspondence is not quite as direct[2].)

Equation (19) therefore may be called a fundamental mechanical equation for a barotropic system and the density a may be given the name density of "proper mechanical energy", abbreviated PME,

$$A=\int_{\text{Vol}} a\,\mathrm{D}V \tag{28}$$

(D differential operator for: element of; V volume). Writing (19) as

$$\frac{\mathrm{d}a}{\mathrm{d}t}=(\Phi+\varphi)\,\frac{\mathrm{d}m}{\mathrm{d}t}\,,$$

and hence with (5)

$$\frac{\mathrm{d}a}{\mathrm{d}t}=-\,(\Phi+\varphi)\,m\operatorname{div}\boldsymbol{v}$$

and adding then $P\operatorname{div}\boldsymbol{v}-P\operatorname{div}\boldsymbol{v}$ on the right-hand side gives

$$\frac{\mathrm{d}a}{\mathrm{d}t}=-\,a\operatorname{div}\boldsymbol{v}+P\operatorname{div}\boldsymbol{v}\,. \tag{29}$$

This is the balance equation of the PME for a barotropic system with, in contrast to (6), only one source term: $P\operatorname{div}\boldsymbol{v}$.

Addition of (7) and (29) results in

$$\frac{\mathrm{d}e}{\mathrm{d}t}=-\,e\operatorname{div}\boldsymbol{v} \tag{30}$$

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[2] The dynamics of a compressible fluid in a gravitational field implies grad $\hat{s}\neq 0$ at least almost everywhere. Because of $\dfrac{\mathrm{d}\hat{s}}{\mathrm{d}t}=\dfrac{\partial\hat{s}}{\partial t}+\boldsymbol{v}\cdot\operatorname{grad}\hat{s}=0$ in general then also is $\dfrac{\partial\hat{s}}{\partial t}\neq 0$ (besides special cases with $\boldsymbol{v}\perp\operatorname{grad}\hat{s}$ everywhere).

with

$$e = u + a \quad \text{and} \quad E = \int_{\text{Vol}} e \, \mathrm{D}V; \tag{31}$$

i.e. E is a conservation quantity for a barotropic system where the potential of the force field may be time-dependent. For this reason the name "proper energy" (abbreviated PE) may be introduced for E.

Comparison of (29) with (6) shows that there is no extra flux term for the PME (and PE), in contradistinction to the common energies with their $P\boldsymbol{v}$. This means an essentially different flux behaviour (discussed in the next section). A consequence is the constancy of the PE of a barotropic system accelerated by external loads (a simple example is given in Sect. VI).

Because of the equivalence of gravitational and inertial mass in all equations for the PME and PE the potentials Φ and φ appear together as a sum. This sum, $\Phi + \varphi$, has the important property to be invariant under transformations between arbitrarily accelerated frames of reference:

In (20) m and P are invariant under these transformations (this paper is nonrelativistic). Hence differences $(\Phi + \varphi) - (\Phi + \varphi)_0$ (for different times or location) are likewise invariant. As will be shown in Sect. VIII (the discussion of (60) and (61)), there is a well-defined zero for $\Phi + \varphi$. Then $\Phi + \varphi$ is also invariant and hence, according to (16), are a and also e, i.e. the PME and PE. This is quite different from the behaviour of the customary mechanical energy, where the kinetic energy and hence the energies containing it already change under Galilean transformations.

In a transformation from an inertial reference frame to an accelerated one with acceleration $\boldsymbol{\beta}(t)$ relative to the former there is grad = grad* (a star signifying the accelerated system). Then from $\Phi^* = \Phi - \boldsymbol{\beta} \cdot \boldsymbol{r}$ follows the acceleration grad* $\Phi^* = \dfrac{\mathrm{d}\boldsymbol{v}^*}{\mathrm{d}t} = \dfrac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} - \boldsymbol{\beta}$ in the new frame. This is compensated by $\varphi^* = \varphi + \boldsymbol{\beta} \cdot \boldsymbol{r}$ with grad* φ^* for the force field, leaving $\Phi + \varphi$ invariant. For a transition to a system rotating around a fixed axis with the velocity $\boldsymbol{\omega} = \boldsymbol{\omega}(t)$, apparent forces enter having no scalar potential. Then $\Phi + \varphi$ necessarily splits according to $(\Phi + \varphi)\,\delta_{ik} = \Phi_{ik} + \varphi_{ik}$ (δ_{ik} component of unit tensor); i.e. the respective potentials become tensorial and divergence operation leads to acceleration and forces (not discussed in this paper).

It may be noted in passing, considering a relativistic generalization, that within the structure introduced in this paper – eliminated momentum, acceleration deriving from a scalar (or tensorial) potential which is closely connected with the potential of the gravitational field – there is no room for something similar to an energy-momentum tensor.

IV. Transport Properties of Customary and Proper Energies

Looking at the customary balance equation (6) for mechanical energy there is a special flux term $P\boldsymbol{v}$ in the second member of the right-hand side. From $-\operatorname{div} P\boldsymbol{v} = -\boldsymbol{v} \cdot \operatorname{grad} P - P \operatorname{div} \boldsymbol{v}$ can be seen that this flux brings (positively or negatively) into a volume element the energy for acceleration and/or change of potential energy (due to grad P) and simultaneously the transformation energy to internal energy (due to div $\boldsymbol{v}$). In the balance equation (29) for the PME there is no such term but only a convective one. In consequence of this, if a material volume is considered, there is no exchange of the PME (and likewise PE) with the surroundings during motion and deformation of a barotropic system.

From the so-called transport theorem of fluid mechanics [1] applied on the PME, and use of (29) follows

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int_{V_{\text{mat}}} a \, \mathrm{D}V = \int_{V_{\text{mat}}} \left(\frac{\mathrm{d}a}{\mathrm{d}t} + a \operatorname{div} \boldsymbol{v} \right) \mathrm{D}V$$

$$= \int_{V_{\text{mat}}} P \operatorname{div} \boldsymbol{v} \, \mathrm{D}V \quad (V_{\text{mat}} \text{ material volume}). \tag{32}$$

Equation (7) leads correspondingly to

$$\frac{\mathrm{d}U}{\mathrm{d}t} = - \int_{V_{\text{mat}}} P \operatorname{div} \boldsymbol{v} \, \mathrm{D}V. \tag{33}$$

Addition of (32) and (33) yields

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int_{V_{\text{mat}}} e \, \mathrm{D}V = 0. \tag{34}$$

For a quasistatic deformation (and grad $P = 0$ everywhere) (32) to (34) reduce to

$$\mathrm{d}A = P \, \mathrm{d}V; \quad \mathrm{d}U = -P \, \mathrm{d}V; \quad \mathrm{d}E = 0.$$

Hence a reversible adiabatic compression (expansion) means a shift from PME to internal energy and vice versa within a material system. A travelling acoustical wave without energy dissipation is an example of a periodic shift between these two energies without transport of PME and PE in contradistinction to the conventional energies and momentum.

V. Relation to Bernoulli's Equation

As before, a barotropic system is considered. Division of the balance equation of PE (30) by that of mol number results in $\frac{\mathrm{d} \ln e/n}{\mathrm{d}t} = 0$ and hence $\frac{\mathrm{d}\hat{e}}{\mathrm{d}t} = \frac{\partial \hat{e}}{\partial t} + \boldsymbol{v} \cdot \operatorname{grad} \hat{e} = 0$, i.e. for a material point there is

$$\hat{e} = (\Phi + \varphi)\, \hat{m} + P\hat{v} + \hat{u} = (\Phi + \varphi)\, \hat{m} + \hat{h} = \text{const} \quad \text{(on a path)} \tag{35}$$

($\hat{e}$, $\hat{m}$, $\hat{v} = 1/n$, $\hat{u}$, $\hat{h} = \hat{u} + P\hat{v}$ molar PE, mass, volume, internal energy, enthalpy, respectively).

If additionally the system is stationary, then because of the coincidence of pathlines and streamlines $\hat{e} = \text{const}$ (along a streamline). From

$$\operatorname{grad} \Phi = \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \operatorname{grad} \boldsymbol{v}$$

$$= \frac{\partial \boldsymbol{v}}{\partial t} + \operatorname{grad} \frac{\boldsymbol{v}^2}{2} - \boldsymbol{v} \times \operatorname{curl} \boldsymbol{v}$$

results for a stationary flow field and integration along a streamline $\Phi = \frac{\boldsymbol{v}^2}{2} + \text{const}$ (along a streamline). This, introduced into (35), yields Bernoulli's equation

$$\left(\frac{\boldsymbol{v}^2}{2} + \varphi\right) \hat{m} + \hat{h} = \text{const (along a streamline).} \tag{36}$$

VI. The Case of Incompressibility

In the limiting case of incompressibility with additionally $\operatorname{grad} m = 0$ everywhere, i.e. $m(\boldsymbol{r}, t) = \text{const}$, (9) is trivially fulfilled. Coupling between PME and internal energy then is absent and therefore thermodynamics eliminated. According to (19) now already for PME density is $a(\boldsymbol{r}, t) = (\Phi + \varphi)\, m + P = \text{const}$ for a system in any state of motion.

As this behaviour is so different from the one of conventional mechanical energy a simple example may be given: the acceleration of a cylindrical column of length L of an incompressible liquid in a time-independent gravitational field, $\frac{\partial \varphi}{\partial x} = g = \text{const}$, $\frac{\partial \varphi}{\partial t} = 0$, in an open container of negligible mass; acceleration and axis of the cylinder parallel to field direction coinciding with coordinate x; outside the container everywhere $P = 0$; at the bottom of the container a constant load acting from $t = 0$ on, effecting there $P = P_0$ (together with the gravitational field); the bottom being at $x = 0$ for $= 0$.

Then there is $\frac{\partial P}{\partial x} = -\frac{P_0}{L}$, because of constant acceleration and $P(L) = 0$. From (4) follows $\frac{\partial \Phi}{\partial x} = \frac{\mathrm{d}v}{\mathrm{d}t} = \frac{P_0}{mL} - g$ and hence $v = \left(\frac{P_0}{mL} - g\right) t$ (with $v_0 = 0$ for $t = 0$) and $x = \left(\frac{P_0}{mL} - g\right) \frac{t^2}{2} + X$ with $0 \leq X \leq L$ position for $t = 0$. Because of $\frac{\partial P}{\partial x} = \text{const}$ together with the constant boundary conditions, there is

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} = 0$$

and hence

$$\frac{\partial P}{\partial t} = \left(\frac{P_0}{mL} - g\right) \frac{P_0}{L}\, t\,.$$

From (22) with $\frac{\partial \varphi}{\partial t} = 0$ results

$$\frac{\partial \Phi}{\partial t} = -\left(\frac{P_0}{mL} - g\right) \frac{P_0}{mL}\, t\,.$$

Then

$$\mathrm{d}\Phi = \frac{\partial \Phi}{\partial x} \mathrm{d}x + \frac{\partial \Phi}{\partial t} \mathrm{d}t$$

$$= \left(\frac{P_0}{mL} - g\right) \mathrm{d}x - \left(\frac{P_0}{mL} - g\right) \frac{P_0}{mL}\, t\, \mathrm{d}t$$

gives after integration

$$\Phi - \Phi_0 = \left(\frac{P_0}{mL} - g\right)\left(x - \frac{P_0 t^2}{2mL}\right)$$

$$= \left(\frac{P_0}{mL} - g\right)\left(X - \frac{g t^2}{2}\right)$$

with $\Phi = \Phi_0$ for $x = 0$, $t = 0$. For the pressure results correspondingly

$$P - P_0 = -\frac{P_0}{L}\left\{x - \left(\frac{P_0}{mL} - g\right) \frac{t^2}{2}\right\} = -\frac{P_0}{L} X\,.$$

The latter two relations together with

$$\varphi - \varphi_0 = g x = g\left\{\left(\frac{P_0}{mL} - g\right) \frac{t^2}{2} + X\right\}$$

introduced in (16) results in $a(x, t) = (\Phi_0 + \varphi_0)\, m + P_0 = a(x=0,\ t=0)$, as it should.

VII. Extension to Irreversible Systems

For cases of linear-, cylindric-, or spheric-symmetry of multicomponent systems with heat conduction, diffusion and chemical reactions trivially, there is curl $\dfrac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = 0$, i.e. there exists an acceleration potential Φ. The term in parentheses of (13), written in the form $\dfrac{\partial m}{\partial t}\dfrac{\partial m}{\partial x}\left(\dfrac{\partial P}{\partial x}\dfrac{\partial x}{\partial m} - \dfrac{\partial P}{\partial t}\dfrac{\partial t}{\partial m}\right)$, now vanishes because for $P(x, t) = P\{y_1(x, t), \ldots, y_n(x, t)\}$ there is

$$\frac{\partial P}{\partial x}\frac{\partial x}{\partial y_k} = \sum_i \frac{\partial P}{\partial y_i}\frac{\partial y_i}{\partial x}\frac{\partial x}{\partial y_k} = \frac{\partial P}{\partial y_k}$$

and likewise

$$\frac{\partial P}{\partial t}\frac{\partial t}{\partial y_k} = \frac{\partial P}{\partial y_k}$$

with $m = y_k$ as one of the independent variables. Therefore (14) to (20), (22) and (23) are valid also for more than one free variable, with the distinction, however, that (19) and (20) are not integrable now.

Equation (24) has to be substituted by

$$\mathrm{d}u = T\,\mathrm{d}s + \sum \mu_\alpha\, \mathrm{d}n_\alpha \tag{37}$$

(index α signifying substances), and (25) by

$$u = T s - P + \sum n_\alpha \mu_\alpha\,. \tag{38}$$

Addition of (19) and (37) leads to

$$\mathrm{d}e = T\,\mathrm{d}s + \sum \{(\Phi + \varphi)\, \hat{m}_\alpha + \mu_\alpha\}\, \mathrm{d}n_\alpha \tag{39}$$

(not integrable), where $m = \sum \hat{m}_\alpha n_\alpha$ ($\hat{m}_\alpha$ molar mass of substance α) has been used; addition of (16) and (38) to

$$e = T s + \sum \{(\Phi + \varphi)\, \hat{m}_\alpha + \mu_\alpha\}\, n_\alpha\,. \tag{40}$$

From (39) and (40) follows

$$s\,\mathrm{d}T + \sum n_\alpha\, \mathrm{d}\{(\Phi + \varphi)\, \hat{m}_\alpha + \mu_\alpha\} = 0\,. \tag{41}$$

(not integrable).

In view of the vector notation of this section one should remember the symmetry-restrictions introduced above.

The balance equation for the mol-number N_α of substance α is given by

$$\frac{\mathrm{d}n_\alpha}{\mathrm{d}t} = -\, n_\alpha \operatorname{div} \boldsymbol{v} - \operatorname{div} \boldsymbol{j}_\alpha + \pi_\alpha \tag{42}$$

with $\boldsymbol{j}_\alpha = n_\alpha(\boldsymbol{v}_\alpha - \boldsymbol{v})$ the diffusional flux of substance α ($\boldsymbol{v}_\alpha$ its velocity, related to $\boldsymbol{v}$ by $m\boldsymbol{v} = \sum n_\alpha \hat{m}_\alpha \boldsymbol{v}_\alpha$); $\sum \hat{m}_\alpha \boldsymbol{j}_\alpha = 0$; π_α source term according to chemical reactions.

The diffusional fluxes of the distinct quantities Y are given by $\sum \hat{y}_\alpha \boldsymbol{j}_\alpha$ with $\hat{y}_\alpha = \left(\dfrac{\partial Y}{\partial N_\alpha}\right)_{T,\,P,\,N_\beta \neq N_\alpha}$ the partial molar quantities of the respective Y; density $y = \sum n_\alpha \hat{y}_\alpha$. The existence of partial molar quantities for the PME and PE follows from the fact that for $P = \text{const}$ already is $(\Phi + \varphi) = \text{const}$, as is to be seen from (20).

The various balance equations then are (π_Y the respective source term):

for the internal energy U

$$\frac{\mathrm{d}u}{\mathrm{d}t} = -\, u \operatorname{div} \boldsymbol{v} - \operatorname{div}\left(\sum \hat{u}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{q}\right) + \pi_V \tag{43}$$

($\boldsymbol{q}$ heat flux vector);

for the entropy S

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\, s \operatorname{div} \boldsymbol{v} - \operatorname{div}\left(\sum \hat{s}_\alpha \boldsymbol{j}_\alpha + \frac{\boldsymbol{q}}{T}\right) + \pi_S\,; \tag{44}$$

for the PME

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\, a \operatorname{div} \boldsymbol{v} - \operatorname{div} \sum \hat{a}_\alpha \boldsymbol{j}_\alpha + \pi_A\,. \tag{45}$$

As one has to expect the PE to be a general conservation quantity, by addition of (43) and (45) then follows

$$\frac{\mathrm{d}e}{\mathrm{d}t} = -\, e \operatorname{div} \boldsymbol{v} - \operatorname{div}\left(\sum \hat{e}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{q}\right). \tag{46}$$

Introduction of (42), (44), and (46) in (39), formulated with material time derivatives, yields for the entropy source term

$$\pi_S = -\frac{1}{T}\left\{\sum \pi_\alpha \mu_\alpha + \left(\sum \hat{s}_\alpha \boldsymbol{j}_\alpha + \frac{\boldsymbol{q}}{T}\right) \cdot \operatorname{grad} T + \sum \boldsymbol{j}_\alpha \cdot \operatorname{grad}\,[(\Phi + \varphi)\, \hat{m}_\alpha + \mu_\alpha]\right\}. \tag{47}$$

In the first term on the right-hand side $\sum (\Phi + \varphi)\, \hat{m}_\alpha \pi_\alpha$ drops out because of mass conservation. There is no direct term for energy-dissipation due to volume viscosity because this contribution has to be derived from the chemical term $\sum \pi_\alpha \mu_\alpha$ for sufficiently rapid chemical reactions [2]. For a one-component system this contribution derives from non-equilibrium excited states of this one component. (Energy dissipation due to shear viscosity, here absent, results from sufficiently rapid relaxation of tensorial chemical potentials [3].)

In (47) there is one essential difference to an entropy production resulting from the conventional treatment [4]. This is the occurrence of the term $\operatorname{grad}\Phi\hat{m}_\alpha = \hat{m}_\alpha \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}$ in the last term of the right-hand side, i.e. the thermodynamic force of diffusion. The necessity of such a term follows from the equivalence of inertial and heavy mass. The local acceleration contributes, together with the local gravity, to the driving force of diffusion. The occurrence of $\operatorname{grad}\Phi\hat{m}_\alpha$ is characteristic for the new structure introduced in this paper; it cannot occur in the customary treatment. (It is surprising that the local acceleration term $\hat{m}_\alpha \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}$ has never been missed, the more so, as for sedimentation phenomena in rotating systems centrifugal as well as Coriolis forces have to be introduced.)

For thermodynamic equilibrium the conditions

$$\operatorname{grad}\{(\Phi+\varphi)\,\hat{m}_\alpha + \mu_\alpha\} = 0 \tag{48}$$

are necessary but not sufficient, this being a consequence of the non-integrability of (39). The simplest case is: additionally $\operatorname{grad}\Phi = 0$ everywhere and $\operatorname{grad}\varphi$ independent of time.

VIII. A Generalization [3]

Use of the relation between internal energy and mass

$$u = mc^2 \quad (c \text{ velocity of light}), \tag{49}$$

leads to an essential generalization (m is the density which in relativistic context is measured by an observer travelling with the respective material point).

The equations of phenomenological thermodynamics remain unchanged by the inclusion of the latent energy present in matter. To get the correction for the equations concerning the PME it suffices to consider a barotropic system.

Mass now is no more a conservation property. Its balance equation for a barotropic system becomes identical with (7),

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -m\operatorname{div}\boldsymbol{v} + \pi_\mathrm{M} \tag{50}$$

with source term

$$\pi_\mathrm{M} = \frac{\pi_\mathrm{U}}{c^2} = -\frac{P}{c^2}\operatorname{div}\boldsymbol{v}\,. \tag{51}$$

(That for the irreversible case the relation deriving from (50) and (51) is also valid is shown in the text following (78) and (82).)

Taking this into account, there has to be a compensating correction, as (19) and (29) together with (50) instead of (5) are not consistent. To remedy this, a guiding principle is required. To this end the preservation of the form of (19) and (29) is used, connected with a correction of the PME density a.

Introduction of (50) and (51) in (19), written with material derivatives, and addition of $P\operatorname{div}\boldsymbol{v} - P\operatorname{div}\boldsymbol{v}$ on the right-hand side leads to

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\left\{(\Phi+\varphi)\,m + \left(1+\frac{\Phi+\varphi}{c^2}\right)P\right\}\operatorname{div}\boldsymbol{v} + P\operatorname{div}\boldsymbol{v}\,. \tag{52}$$

If now (52) is considered to be the balance equation for a redefined PME (its symbol not changed) then the corrected expression for the PME is given by

$$a = (\Phi+\varphi)\,m + \left(1+\frac{\Phi+\varphi}{c^2}\right)P \tag{53}$$

instead of (16), $\frac{\Phi+\varphi}{c^2}P$ being the correction term.

From (19) (now with the new meaning of PME), and (53) follows

$$\left(m+\frac{P}{c^2}\right)\mathrm{d}(\Phi+\varphi) + \left(1+\frac{\Phi+\varphi}{c^2}\right)\mathrm{d}P = 0 \tag{54}$$

instead of (20), again integrable for a barotropic system:

$$\ln\left(1+\frac{\Phi+\varphi}{c^2}\right) = -\int\frac{\mathrm{d}P}{u+P} + \text{const}\,. \tag{54a}$$

According to (54), the corrected equation of motion is

$$\left(m+\frac{P}{c^2}\right)\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} + \left(1+\frac{\Phi+\varphi}{c^2}\right)\operatorname{grad}P + \left(m+\frac{P}{c^2}\right)\operatorname{grad}\varphi = 0\,. \tag{55}$$

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[3] This generalization is mainly of structural interest. The resulting correction terms are negligible in problems of customary dynamics. This changes, however, if P cannot be neglected beside $u = mc^2$; see section X.

To check the consistency of the generalization (existence of a scalar potential Φ), for (55) there results after some calculation

$$\operatorname{curl}\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \frac{1+\dfrac{\Phi+\varphi}{c^2}}{\left(m+\dfrac{P}{c^2}\right)^2}\operatorname{grad} m \times \operatorname{grad} P\,,$$

which is either zero because of barotropy, $P = P(m)$, or because of the symmetry assumed.

Addition of (53) and (38) yields for the PE

$$\begin{aligned} e &= \left(1+\frac{\Phi+\varphi}{c^2}\right)(u+P) = \left(1+\frac{\Phi+\varphi}{c^2}\right) h \\ &= \left(1+\frac{\Phi+\varphi}{c^2}\right)\left(T s + \sum n_\alpha \mu_\alpha\right). \end{aligned} \tag{56}$$

Use of (49) in (19) and taking into account (37) leads to

$$\mathrm{d}e = \left(1+\frac{\Phi+\varphi}{c^2}\right)\mathrm{d}u = \left(1+\frac{\Phi+\varphi}{c^2}\right)\left(T\,\mathrm{d}s + \sum \mu_\alpha\,\mathrm{d}n_\alpha\right). \tag{57}$$

From (56) and (57) results

$$s\,\mathrm{d}\left\{\left(1+\frac{\Phi+\varphi}{c^2}\right)T\right\} + \sum n_\alpha\,\mathrm{d}\left\{\left(1+\frac{\Phi+\varphi}{c^2}\right)\mu_\alpha\right\} = 0 \tag{58}$$

or, alternatively written,

$$s\,\mathrm{d}T + \sum n_\alpha\,\mathrm{d}\mu_\alpha + h\,\mathrm{d}\ln\left(1+\frac{\Phi+\varphi}{c^2}\right) = 0\,. \tag{59}$$

Equations (58) and (59) are different forms of (54).

From (54a) follows $1+\dfrac{\Phi+\varphi}{c^2} > 0$, therefore, see (56), $e > 0$[4], whereas a, see (53), can be negative.

If the entropy is maximized for an isolated system, i.e. $\delta S = 0$ with $\delta E = 0$ and

$$\int\limits_V \left(\delta n_\alpha - \sum_{\beta=1}^{r} \nu_{\alpha\beta}\,\delta\xi_\beta\right)\mathrm{D}V = 0$$

($\nu_{\alpha\beta}$ stoichiometric coefficient of substance α in reaction β with customary sign convention [5]; ξ_β extent of reaction β per unit of volume; r independent chemical reactions) by use of (57) the conditions necessary for thermodynamic equilibrium result (written slightly transformed):

$$\left(1+\frac{\Phi+\varphi}{c^2}\right)T = \text{const}\,, \tag{60}$$

$$\left(1+\frac{\Phi+\varphi}{c^2}\right)\mu_\alpha = \text{const}\,, \tag{61}$$

and

$$\sum_{\alpha=1}^{k} \nu_{\alpha\beta}\,\mu_\alpha = 0\,, \quad \beta = 1, \ldots, r \tag{62}$$

(k number of substances).

Equations (60) and (61), however, are not sufficient (besides the stability problem) because of the non-integrability of (57). This becomes apparent by introduction of (60) and (61) in the Gibbs-Duhem equation written with gradients,

$$s\operatorname{grad} T + \sum n_\alpha \operatorname{grad}\mu_\alpha - \operatorname{grad} P = 0,$$

and use of (38) and (49), thus leading to the equation of motion (55). Complete equilibrium conditions follow if additionally relative motion within the system is excluded, thus fixing Φ and φ according to the reference system chosen.

The gradient of (60) or (61) evidences that there has to be a well-defined zero for the sum $\Phi+\varphi$, or to put it differently, $\Phi+\varphi$ is an absolute quantity, because otherwise a mere shift of its scale would change the equilibrium.

Neglection of $\dfrac{\Phi+\varphi}{c^2}$ in (60) leads to the ordinary condition of thermal equilibrium. In (61) the procedure has to be different. Because of (49) from

$$u = m c^2 = \sum n_\alpha \hat{m}_\alpha c^2 \quad \text{and}$$
$$u = T s - P + \sum n_\alpha \mu_\alpha \approx \sum n_\alpha \mu_\alpha$$

results $\mu_\alpha \approx \hat{m}_\alpha c^2$. This fact used in (61) leads to condition (48).

IX. Irreversible Systems – The Generalized Case

It is instructive to discuss a one-component system with heat conduction first.

Again the symmetry-restrictions necessary for the existence of a scalar potential Φ should be remembered.

The inclusion of heat conduction already necessitates a revision of the balance equations. Now, because of its momentum there is a contribution of the heat flux vector to the velocity of a material point.

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[4] This is a general outcome because for negative pressures, possible in liquids (and solids), there always is $|P| \ll u$.

Additionally the appearance of $m+\dfrac{P}{c^2}$ in the equation of motion (55) suggests a corresponding extension. For a one-component system the velocity $\boldsymbol{v}$ of a material point then is given by

$$\left(m+\frac{P}{c^2}\right)\boldsymbol{v}=\left(m+\frac{P}{c^2}\right)\boldsymbol{v}^*+\frac{\boldsymbol{q}}{c^2} \tag{63}$$

with $\boldsymbol{v}^*$ the velocity of the matter alone.

An extensive quantity Y (y its density) is transported by $y\boldsymbol{v}^*$ and for most quantities by an additional term y_{rest}. A spatial balance leads to

$$\begin{aligned}\frac{\partial y}{\partial t}&=-\operatorname{div}(y\boldsymbol{v}^*+\boldsymbol{y}_{\text{rest}})+\pi_Y\\&=-\operatorname{div}\{y\boldsymbol{v}+y(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{y}_{\text{rest}}\}+\pi_Y\end{aligned} \tag{64}$$

instead of (1). The material balance, by use of (2), is then given by

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-y\operatorname{div}\boldsymbol{v}-\operatorname{div}\{y(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{y}_{\text{rest}}\}+\pi_Y\,. \tag{65}$$

The individual balances are:

for the internal energy

$$\frac{\mathrm{d}u}{\mathrm{d}t}=-u\operatorname{div}\boldsymbol{v}-\operatorname{div}\{u(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{q}\}+\pi_U\,, \tag{66}$$

for the entropy

$$\frac{\mathrm{d}s}{\mathrm{d}t}=-s\operatorname{div}\boldsymbol{v}-\operatorname{div}\left\{s(\boldsymbol{v}^*-\boldsymbol{v})+\frac{\boldsymbol{q}}{T}\right\}+\pi_S\,, \tag{67}$$

for mol-number

$$\frac{\mathrm{d}n}{\mathrm{d}t}=-n\operatorname{div}\boldsymbol{v}-\operatorname{div}\{n(\boldsymbol{v}^*-\boldsymbol{v})\}\,. \tag{68}$$

For the balance of the PME the introduction of a flux term $\boldsymbol{p}$ proves to be necessary for consistency

$$\frac{\mathrm{d}a}{\mathrm{d}t}=-a\operatorname{div}-\operatorname{div}\{a(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{p}\}+\pi_A\,. \tag{69}$$

With the conservation property of the PE, $\pi_U+\pi_A=0$, addition of (66) and (69) leads to

$$\frac{\mathrm{d}e}{\mathrm{d}t}=-e\operatorname{div}\boldsymbol{v}-\operatorname{div}\{e(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{p}+\boldsymbol{q}\}\,. \tag{70}$$

To get the source term for the entropy π_S, (67), (68), and (70) have to be introduced in (57) written with material derivatives for a one-component system. Then, after a simple calculation there is

$$\begin{aligned}&\left\{e-\left(1+\frac{\Phi+\varphi}{c^2}\right)(Ts+n\mu)\right\}\operatorname{div}\boldsymbol{v}\\&+\operatorname{div}\left\{(\boldsymbol{v}^*-\boldsymbol{v})\left[e-\left(1+\frac{\Phi+\varphi}{c^2}\right)(Ts+n\mu)\right]\right.\\&\left.+\boldsymbol{p}-\frac{\Phi+\varphi}{c^2}\boldsymbol{q}\right\}+(\boldsymbol{v}^*-\boldsymbol{v})\left\{n\operatorname{grad}\left(1+\frac{\Phi+\varphi}{c^2}\right)\mu\right.\\&\left.+s\operatorname{grad}\left(1+\frac{\Phi+\varphi}{c^2}\right)T\right\}+\frac{\boldsymbol{q}}{T}\operatorname{grad}\left(1+\frac{\Phi+\varphi}{c^2}\right)T\\&+\left(1+\frac{\Phi+\varphi}{c^2}\right)T\pi_S=0.\end{aligned}$$

Because of (56) the first term vanishes and likewise the first term in the second curled brackets. For the third term the same follows from (58).

Entropy production then amounts to

$$\pi_S=-\frac{\boldsymbol{q}}{\left(1+\dfrac{\Phi+\varphi}{c^2}\right)T^2}\operatorname{grad}\left(1+\frac{\Phi+\varphi}{c^2}\right)T \tag{71}$$

if the condition

$$\boldsymbol{p}-\frac{\Phi+\varphi}{c^2}\boldsymbol{q}=0 \tag{72}$$

is fulfilled. Looking at (60), something like (71) is to be expected. Therefore (72) must be the relation which connects $\boldsymbol{p}$ and $\boldsymbol{q}$.

For the flux term in arched brackets of (66) follows from (63) and (49)

$$u(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{q}=-P(\boldsymbol{v}^*-\boldsymbol{v})=+\frac{P}{mc^2+P}\boldsymbol{q}\,. \tag{73}$$

For the corresponding term in (69), by additional use of (53) and (72) results

$$a(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{p}=-\frac{P}{mc^2+P}\boldsymbol{q}\,. \tag{74}$$

Then in (70) there is

$$e(\boldsymbol{v}^*-\boldsymbol{v})+\boldsymbol{p}+\boldsymbol{q}=0; \tag{75}$$

i.e. $\dfrac{\mathrm{d}e}{\mathrm{d}t}=-e\operatorname{div}\boldsymbol{v}$ as in the reversible case, (30). The same is valid for multicomponent systems with additionally diffusion and chemical reactions (to be treated briefly at the end of this section). Therefore it can be stated: Any irreversible change, in particular heat conduction, in systems where a potential Φ applies, does not effect exchange of PE between material parts of the system.

On first sight this may appear surprising. One has, however, to bear in mind the meaning of a material volume deriving from the definition of the velocity $\boldsymbol{v}$ of a material point, (63) and (80) respectively.

For completeness the corresponding results for the nonconvective term in (67)

$$s(\boldsymbol{v}^* - \boldsymbol{v}) + \frac{\boldsymbol{q}}{T} = \left(\frac{u + P - T s}{m c^2 + P}\right) \frac{\boldsymbol{q}}{T} = \frac{n \mu}{m c^2 + P} \frac{\boldsymbol{q}}{T}, \tag{76}$$

and in (68)

$$n(\boldsymbol{v}^* - \boldsymbol{v}) = -\frac{n}{m c^2 + P} \boldsymbol{q}, \tag{77}$$

may be given.

If (66) and (70) are introduced in (57) (written with material time derivatives), use of (56), (73), and (75) yields

$$\pi_U = -P \operatorname{div} \boldsymbol{v} - \operatorname{div} P(\boldsymbol{v}^* - \boldsymbol{v}) = -\pi_A. \tag{78}$$

As (52) to (58) have been employed for the irreversible case in this section, though so far only based on (50) together with (51),

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -m \operatorname{div} \boldsymbol{v} - \frac{P}{c^2} \operatorname{div} \boldsymbol{v},$$

i.e. substantiated for barotropy, its extended applicability has to be checked. Introduction of (73) and (78) in the last two members of (66) shows that indeed there is

$$-\operatorname{div}\{u(\boldsymbol{v}^* - \boldsymbol{v}) + \boldsymbol{q}\} + \pi_U = -P \operatorname{div} \boldsymbol{v}, \tag{79}$$

thus by division with c^2 and use of (49) transforming (66) into the foregoing relation.

Finally diffusion and chemical reactions are included in the discussion.

Equation (63) has to be substituted by

$$\left(m + \frac{P}{c^2}\right) \boldsymbol{v} = \sum \left(m_\alpha + n_\alpha \hat{v}_\alpha \frac{P}{c^2}\right) \boldsymbol{v}_\alpha + \frac{\boldsymbol{q}}{c^2} \tag{80}$$

with the partial mass density $m_\alpha = n_\alpha \hat{m}_\alpha$, $\sum m_\alpha = m$, and the partial molar volume $\hat{v}_\alpha$, $\sum n_\alpha \hat{v}_\alpha = 1$. For the diffusional fluxes $\boldsymbol{j}_\alpha = n_\alpha(\boldsymbol{v}_\alpha - \boldsymbol{v})$, instead of $\sum \hat{m}_\alpha \boldsymbol{j}_\alpha = 0$ now, because of (80), there is

$$\sum \left(\hat{m}_\alpha + \frac{P \hat{v}_\alpha}{c^2}\right) \boldsymbol{j}_\alpha + \frac{\boldsymbol{q}}{c^2} = 0.$$

The form of the balance equations (42), (43), and (44) remains unchanged. In (45) the second term on the right-hand side now is: $\operatorname{div}\left(\sum \hat{a}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{p}\right)$, and the corresponding term in (46): $\operatorname{div}\left(\sum \hat{e}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{p} + \boldsymbol{q}\right)$. Equation (72) applies unchanged.

Corresponding to (73) and (74) there is

$$\sum \hat{u}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{q} = -\sum P \hat{v}_\alpha \boldsymbol{j}_\alpha = -\sum \hat{a}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{p}. \tag{81}$$

The first relation of (81) directly follows from (80); for the second, (72) and the partial molar PME

$$\hat{a} = \frac{\Phi + \varphi}{c^2} \hat{u}_\alpha + \left(1 + \frac{\Phi + \varphi}{c^2}\right) P \hat{v}_\alpha$$

(following from (53) with (49)) and the first relation have to be applied. For a one-component system, (81) reduces to (73) and (74). Because of (81) in generalization of (75), likewise is

$$\sum \hat{e}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{p} + \boldsymbol{q} = 0. \tag{82}$$

Now, application of (43) and the revised (46) in (57) (formulated with material time derivatives) and then of (56) and (82) gives the generalization of (79):

$$-\operatorname{div}\left(\sum \hat{u}_\alpha \boldsymbol{j}_\alpha + \boldsymbol{q}\right) + \pi_U = -P \operatorname{div} \boldsymbol{v}. \tag{83}$$

The balance equations (42), (44), and (46), the latter with an additional $\boldsymbol{p}$ as given above, introduced in (57), written with material derivatives and use of (72), leads to the entropy production

$$\pi_S = -\frac{1}{T} \sum \pi_\alpha \mu_\alpha - \frac{1}{\left(1 + \frac{\Phi + \varphi}{c^2}\right) T} \left\{\left(\sum \hat{s}_\alpha \boldsymbol{j}_\alpha + \frac{\boldsymbol{q}}{T}\right) \cdot \operatorname{grad}\left(1 + \frac{\Phi + \varphi}{c^2}\right) T + \sum \boldsymbol{j}_\alpha \cdot \operatorname{grad}\left(1 + \frac{\Phi + \varphi}{c^2}\right) \mu_\alpha\right\}. \tag{84}$$

By use of the approximations discussed in the context of (60) and (61), the entropy production (84) reduces to (47).

Elimination of $\operatorname{grad}\left(1 + \frac{\Phi + \varphi}{c^2}\right)$ in (84) by use of (54) leads to

$$\pi_S = -\frac{1}{T} \sum \pi_\alpha \mu_\alpha - \frac{1}{T} \left\{\left(\sum \hat{s}_\alpha \boldsymbol{j}_\alpha + \frac{\boldsymbol{q}}{T}\right) \cdot \left(\operatorname{grad} T - \frac{T}{u + P} \operatorname{grad} P\right) + \sum \boldsymbol{j}_\alpha \cdot \left(\operatorname{grad} \mu_\alpha - \frac{\mu_\alpha}{u + P} \operatorname{grad} P\right)\right\}.$$

The additional term, $-\frac{T}{u + P} \operatorname{grad} P$, in the driving force of heat conduction, known as a result of relativistic irreversible dynamics [6a], here derives from a nonrelativistic context.

From conventional irreversible dynamics results as driving force of diffusion:

$$\operatorname{grad}(\mu_\alpha + \hat{m}_\alpha \varphi) = \operatorname{grad} \mu_\alpha - \left(\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} + \frac{1}{m} \operatorname{grad} P\right) \hat{m}_\alpha ;$$

here it is given by

$$\operatorname{grad} \mu_\alpha - \frac{\mu_\alpha}{u+P} \operatorname{grad} P \quad \text{with} \quad \frac{\mu_\alpha}{u+P} \approx \frac{\hat{m}_\alpha}{m} .$$

X. Application to Blackbody Radiation

For blackbody radiation (24), (25), and (26) reduce to

$$\mathrm{d}u = T\,\mathrm{d}s , \tag{85}$$

$$u = T s - P , \tag{86}$$

and

$$s\,\mathrm{d}T - \mathrm{d}P = 0 . \tag{87}$$

At very high temperatures there is pair production. The above equations remain valid for particle/radiation equilibrium, the chemical potentials of the particles being zero.

Systems of this kind depend on one variable and therefore represent barotropic ones. (A matterfree radiation field according to (49) has mass density and hence local inertia.)

Integration in (54a) by use of (86) and (87) leads to

$$\left(1 + \frac{\Phi + \varphi}{c^2}\right) T = \vartheta , \tag{88}$$

an expression like (60), here, however, not resulting from maximizing the overall entropy but directly as an intrinsic property of the system. (88) is an equation of state, the constant ϑ being an universal one; $\vartheta > 0$ because of $1 + \dfrac{\Phi + \varphi}{c^2} > 0$.

Use of (86) to (88) in (53) yields

$$a = (\vartheta - T)\, s + P = (\vartheta - T) \frac{\mathrm{d}P}{\mathrm{d}T} + P ; \tag{89}$$

from (56) follows

$$e = \vartheta s = \vartheta \frac{\mathrm{d}P}{\mathrm{d}T} . \tag{90}$$

By (90) the invariance of the PE against transformations between arbitrarily accelerated frames of reference becomes transparent, because the entropy of a system is distinguished by this property.

For $T \to \infty$ in (89) there is $a \to -u$; e becoming infinite too, but of lower order.

For blackbody radiation,

$$u = 3P = \alpha T^4 \tag{91}$$

(α Stefan-Boltzmann constant), (89) gives

$$a = \left(\frac{4\vartheta}{3T} - 1\right) \alpha T^4 \tag{92}$$

and (90)

$$e = \frac{4}{3} \alpha \vartheta T^3 . \tag{93}$$

According to (92) the PME is negative for $T > \frac{4}{3}\vartheta$. For $T = \vartheta$, i.e. $\Phi + \varphi = 0$, the PME is maximal.

The dynamics of sedimentation of blackbody radiation in a changing field of gravitation and/or acceleration of a system is governed by the equation of motion

$$\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} + \operatorname{grad} \varphi + \frac{c^2 \vartheta}{T^2} \operatorname{grad} T = 0 , \tag{94}$$

following from (55) by use of (86) to (88) [5].

If for given conditions, say $\operatorname{grad} \Phi = \dfrac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = 0$ and $\operatorname{grad} \varphi = \boldsymbol{g}$, grad T can be measured, ϑ would be obtainable, and with it the blackbody radiation data of $\Phi + \varphi$, a, and e in their dependence on temperature.

The second equation necessary for handling a problem of motion is the one resulting from (50) and (51), which with (49) and (85) to (87) transforms to

$$\frac{\mathrm{d}\dfrac{\mathrm{d}P}{\mathrm{d}T}}{\mathrm{d}t} = -\frac{\mathrm{d}P}{\mathrm{d}T} \operatorname{div} \boldsymbol{v} ;$$

this with (91) gives

$$\frac{\mathrm{d}T}{\mathrm{d}t} + \frac{T}{3} \operatorname{div} \boldsymbol{v} = 0 . \tag{95}$$

For blackbody radiation (94) and (95), resulting from the corrected equations (55) and (50), are notably different from the ones resulting from (4) and (5) with (49). Instead of $\dfrac{c^2 \vartheta}{T^2} \operatorname{grad} T$ then there is the term $\dfrac{4c^2}{3T} \operatorname{grad} T$, instead of $\dfrac{T}{3} \operatorname{div} \boldsymbol{v}$ the term $\dfrac{T}{4} \operatorname{div} \boldsymbol{v}$.

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[5] The velocity $\boldsymbol{v}$ here is given by (63) with $\boldsymbol{v}^*$ dropping out. The remaining equation $(u+P)\,\boldsymbol{v} = T s\,\boldsymbol{v} = \boldsymbol{q}$ relates $\boldsymbol{v}$ with a heat flux vector, now of convective character. (That there is no entropy production follows from (71) and (88).)

XI. Conclusions

The dynamics of continuous systems in a gravitational field (time-dependent potential φ allowed) with existing acceleration potential Φ is discussed, necessitating either dependence of pressure on one variable only (barotropy, reversibility) or, for irreversible systems, dependence on but one spatial coordinate. Under these conditions there exists what, in analogy to thermodynamics, is called a fundamental equation of continuum mechanics, being integrable for barotropic systems, not integrable for irreversible ones. In the first case the future state of a system only depends on the initial and the mechanical boundary conditions and, if the occasion arises, on $\varphi(t)$; in the other case the path of development comes in via the irreversibility.

The sum $\Phi + \varphi$ possesses a well-defined zero, is an invariant with regard to arbitrarily accelerated frames of references (at least in the nonrelativistic domain), and is an integral part of a quantity named proper mechanical energy (PME) likewise invariant under the named conditions. The latter together with internal energy constitutes a quantity, named proper energy (PE), which besides its more general conservation property and its invariance differs from conventional energy by the way of its conservation. A material volume undergoing an arbitrary process with its surroundings (deformation, acceleration, heat transfer, diffusion) does not change its PE.

A missing term in the driving force of diffusion originating from the acceleration field, not derivable by use of conventional continuum mechanics, is provided by the equations for the PME, see (47) and (84), and likewise a new relation for blackbody radiation, (88).

An interesting aspect is that the PME can be negative.

Properties and results of the structure expounded are of such a nature that one has to expect a general theoretical frame which comprehends the regime discussed as a special case. The search for generalization necessarily leads to the idea of tensorial acceleration potentials as becomes already apparent with the transformation problem discussed at the end of Section III. The close analogy of the restricted fundamental equations for continuum mechanics to the corresponding equations of thermodynamics (see III) strongly suggests the use of generalized thermodynamics [3] with tensorial chemical potentials as a model. This will be done in a following paper.

In the mechanics with PME and PE, momentum plays a secondary role, kinetic energy is eliminated. This makes it unsuited for mass point mechanics and problems sufficiently reducible to it. During an elastic collision of two solid spheres, for example, in any reference frame the PE of each body does not change, and the PME of each body is the same before and after collision [6] (the generalization to the case of elastic deformation taken for granted).

The generalized conditions of thermodynamic equilibrium, (60) and (61), partly coincide with approximations from relativistic thermodynamics for $|\boldsymbol{v}| \ll c$ and weak gravitational field [6b]. The difference lies in the occurrence of the acceleration potential Φ. A better name for this quantity would be potential of inertia.

The close connection of Φ and φ, inertia and gravity, in all the relations concerned on the one hand is in the spirit of relativity; on the other hand, with regard to a relativistic generalization of the structure presented, it does not fit in the structure of the theory of relativity in its accepted form. It does not admit a Lagrangian density and an energy-momentum tensor.

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[6] For spheres idealized to mass points undergoing elastic collisions in an otherwise empty space Newtonian dynamics for a particle during motion gives $\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = -\operatorname{grad}\varphi$ or $\operatorname{grad}(\Phi+\varphi)=0$, and hence $\Phi+\varphi=\text{const}$. The constant gets back its value after a collision, thus showing the comparative emptiness of this structure for mass point mechanics.

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