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GIBBS' STATISTICAL MECHANICS IN THE THEORY OF RELATIVITY

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Synopsis

Recent investigations in relativistic thermodynamics have shown that the momentum and energy of transferred heat in a thermodynamical process transform as the components of a four-vector under Lorentz transformations, in striking contrast to the ideas of the early formulation of relativistic thermodynamics of sixty years ago. In the present paper it is shown that the results of the new formulation are supported in all details by a relativistic generalisation of Gibbs' classical statistical mechanics.

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1. Introduction and Survey

In a most interesting paper by H. Ott from 1963 [1], it was shown that the old relativistic treatment of thermodynamical processes by Planck and others [2] contained an error which led to a wrong transformation formula for the heat energy transferred in a process. In pre-relativistic thermodynamics, the first law expresses the law of conservation of energy when heat energy is involved in the process. In relativity theory, this law has to be supplemented by a similar law of conservation of momentum. Thus, in an arbitrary system of inertia S, we have four conservation equations*

$$\Delta G_i = \Delta I_i + \Delta Q_i, \quad i = 1,2,3,4 \tag{1.1}$$

with

$$\left.\begin{aligned} \Delta G_i &= \{\Delta \boldsymbol{G}, -\Delta H/c\} \\ \Delta I_i &= \{\Delta \boldsymbol{I}, -\Delta A/c\} \\ \Delta Q_i &= \{\Delta \boldsymbol{Q}, -\Delta Q/c\}. \end{aligned}\right\} \tag{1.2}$$

Here, $\Delta \boldsymbol{G}$ and ΔH are the changes of the momentum $\boldsymbol{G}$ and energy H of the thermodynamic body in a process leading from one equilibrium state to another such state. $\Delta \boldsymbol{I}$ is the mechanical impulse, i.e. the time integral of the mechanical forces acting on the body, while ΔA is the work performed by these forces during the process. Consequently, ΔQ is the heat energy transferred to the body in the process (definition!) and $\Delta \boldsymbol{Q}$ is the corresponding momentum transferred along with the heat supply.

In his paper, quoted above, Ott clearly pointed out that the error in the old treatments is due to a wrong expression for the mechanical work performed by the external forces. However, his argument and his results were not universally recognized and his paper gave rise to a large number

* Latin indices run from 1 to 4, Greek indices from 1 to 3. The metric tensor in Minkowski space has signature +2 and the usual summation convention is made.

of mutually contradicting papers on the subject [3]. Therefore in a recent paper [4], the present author considered once more in all details the simple case of thermodynamical processes in a fluid enclosed in a container of changeable volume. If we assume that the fluid cannot withstand shear, the external force on the fluid is simply the normal pressure from the walls of the container. Since the pressure is a relativistic scalar, it is easy in this case to write down the transformation equations for the quantities ΔG_i and ΔI_i. Then, the transformation laws for the quantities ΔQ_i follow from (1.2). The main results obtained in reference 4 are the following. In general, neither ΔG_i nor ΔI_i will transform like the components of 4-vectors under Lorentz transformations. Nevertheless, the differences $\Delta G_i - \Delta I_i$, i.e. *the ΔQ_i are the covariant components of a 4-vector, the four-momentum of supplied heat.* This result, which in reference 4 was proved for a fluid only, has been shown by Brevik [5] and by Söderholm [6] to be valid for any elastic body and for any thermodynamical process leading from one equilibrium state to another such state of the body.

Further it was shown in reference 4 that the four-momentum of supplied heat for an infinitesimal *reversible* process is proportional to the four-velocity

$$V_i = \{\gamma \boldsymbol{v}, -\gamma c\}, \quad \gamma = (1 - v^2/c^2)^{-1/2} \tag{1.3}$$

of the body:

$$dQ_i^{\text{rev}} = \frac{dQ^0_{\text{rev}}}{c^2} V_i, \tag{1.4}$$

where dQ^0_{rev} is the transferred heat energy measured in the rest system S^0 of the body. The fourth component of (1.4) gives

$$dQ^{\text{rev}} = \frac{dQ^0_{\text{rev}}}{\sqrt{1 - v^2/c^3}}. \tag{1.5}$$

As regards the second law of thermodynamics, it is generally agreed that the entropy S is a relativistic invariant,

i.e.

$$S = S^0, \tag{1.6}$$

and, in the rest system, we have

$$dS^0 = \frac{dQ^0_{\text{rev}}}{T^0} \tag{1.7}$$

where T^0 is the proper temperature as measured in the rest system. If one wants a similar equation

$$dS = \frac{dQ_{\text{rev}}}{T} \tag{1.8}$$

to hold in any other system of inertia, one finds by (1.5–8) that the so defined temperature T is connected with the proper temperature T^0 by OTT's formula

$$T = \frac{T^0}{\sqrt{1 - v^2/c^2}}. \tag{1.9}$$

Thus, T is not an invariant but rather the fourth component of a time-like vector

$$T_i = \frac{T^0}{c} V_i \tag{1.10}$$

the 'temperature 4-vector' introduced by ARZÉLIÈS [7]:

$$T = T^4 = -T_4 \tag{1.11}$$

Obviously the norm of this vector is equal to the invariant proper temperature T^0, since

$$\sqrt{-T_i T^i} = T^0. \tag{1.12}$$

Thus, instead of using a single quantity T, defined by (1.9), for the characterization of the thermodynamic state (together with 'extensive' quantities like the volume etc.) it seems more appropriate in an arbitrary system of inertia to use the four components of the temperature 4-vector T_i for this purpose. Only in the rest system S^0 where the spatial components $T_\iota^0 = 0$ we are left with a single quantity $T_4^0 = -T^0$ as in classical thermodynamics. This point of view was carried through in a recent paper [8] in which also a generally relativistic formulation was given which in a very simple way leads to Tolman's condition for thermal equilibrium in a large body under the influence of its own gravitational field.

However, in the case of an *irreversible* process the formulation of the second law leads to unnecessary complications in this scheme. In the rest system S^0 we have, for an irreversible process,

$$dS^0 > \frac{dQ^0}{T^0}, \tag{1.13}$$

but in an arbitrary system of inertia S, (1.13) is *not* equivalent to

$$dS > \frac{dQ}{T}, \tag{1.14}$$

a relation which is simply not true. This is connected with the fact that the 4-vector dQ_i for irreversible processes is not proportional to V_i in general. However, we get a very simple general formulation of the second law if we, instead of the temperature 4-vector T_i, introduce the reciprocal temperature 4-vector θ^i defined by

$$\theta^i = \theta^0 V^i, \qquad \theta^0 \equiv (T^0)^{-1} \tag{1.15}$$

which has the norm

$$\theta \equiv \sqrt{-\theta_i \theta^i}/c = \theta^0. \tag{1.16}$$

Then, the second law in an arbitrary system S takes the form

$$dS \geqslant -\theta^i dQ_i, \tag{1.17}$$

where the equality sign holds for reversible processes only. In the latter case, where dQ_i is of the form (1.4), (1.17) is identical with (1.7) (or (1.8)) and, for an irreversible process, we have

$$-\theta^i dQ_i = -\theta^{0i} dQ_i^0 = -\frac{c}{T^0} dQ_4^0 = \frac{dQ^0}{T^0}$$

so that (1.17) is equivalent to (1.13). In the form (1.17), the second law can immediately be taken over into the general theory of relativity and the results obtained in reference 8, in particular Tolman's equilibrium conditions, follow immediately.

The considerations in references 4 and 8 were purely thermodynamical, but it is clear that the results quoted in this section should be obtainable also by means of a relativistic generalization of Gibbs' statistical mechanics in which the thermodynamic properties of a macroscopic system in thermal equilibrium is described as mean values in a canonical ensemble. A *reversible* process is then described by a succession of canonical ensembles with varying values for the parameters that characterize the ensemble. In this way it is possible to derive all the earlier mentioned thermodynamic properties of the systems, in particular the transformation properties of ΔG_i, ΔI_i and ΔQ_i, from statistical mechanical considerations, and this is the subject of the present paper.

In view of the generality of the properties in question, it is sufficient to treat a highly simplified model like an ideal gas of equal particles enclosed in a container. Since the particles do not interact in this case, the particles move independently of each other in the field of force originating from the walls of the container and possibly from other external sources. In the next section we shall, therefore, start by considering a one-particle system, which is then easily generalized to the case of n identical particles. It will be shown that the equations of motion can be written in the Hamiltonian form in any system of inertia, but the Hamiltonian will in general not be a constant of the motion. Section 3 contains a short survey of the properties of relativistic phase-spaces, such as Liouville's theorem in an arbitrary Lorentz system and the relativistic invariance of the volume of phase-space. In section 4 we consider ensembles of mechanical systems in the phase-space of an arbitrary Lorentz system. In particular, the relativistic invariance of the probability density and the general form of the latter for a *canonical* ensemble are considered.

The following section contains a derivation of the transformation properties of the mean values of the canonical four-momentum, the forces, the rate of work, and the 'probability exponential' in a canonical ensemble. In section 6 we give a statistical description of a reversible process and a calculation of the mechanical impulse and work is carried out, by which typical relativistic effects are clearly brought out. We shall also obtain a statistical expression for the four-momentum of supplied heat in a reversible process. Finally, in the last section, a number of theorems are derived which allow to calculate mean values of important physical quantities by differentiations of a function that is closely related to the free energy of thermodynamics.

2. Lagrangian and Hamiltonian Form of the Equations of Motion in the Case when the Field of Force is Static in a Certain System of Inertia S^0

The motion of a particle of constant rest mass m subjected to a force $\mathfrak{F}$ in any system of inertia S is generally given by Minkowski's equations

$$\frac{dp_i}{d\tau} = F_i, \quad i = 1,2,3,4, \tag{2.1}$$

where

$$d\tau = dt\sqrt{1 - u^2/c^2} \tag{2.2}$$

is the proper time,

$$p_i = \{\boldsymbol{p}, \ -E/c\} = \left\{\frac{m\boldsymbol{u}}{\sqrt{1 - u^2/c^2}}, \ -\sqrt{m^2c^2 + p^2}\right\} \tag{2.3}$$

is the four-momentum and

$$F_i = \left\{\frac{\mathfrak{F}}{\sqrt{1 - u^2/^2c}}, \ -\frac{(\mathfrak{F}\cdot\boldsymbol{u})/c}{\sqrt{1 - u^2/c^2}}\right\} \tag{2.4}$$

the four-force.

We shall now in particular consider the case where the force $\mathfrak{F}^0$ is static in a certain system S^0 and derivable from a potential $U^0(\boldsymbol{x}^0)$ which is independent of t^0, i.e.

$$\left.\begin{aligned} \mathfrak{F}^0 &= -\operatorname{grad} U^0 \\ F_i^0 &= \left\{-\frac{\partial U^0}{\partial \boldsymbol{x}^0}, \ \left(\frac{\partial U^0}{\partial \boldsymbol{x}^0}\cdot \boldsymbol{u}^0/c\right)\right\}/\sqrt{1 - u^{02}/c^2}. \end{aligned}\right\} \tag{2.5}$$

$U^0 = U^0(\boldsymbol{x}^0, a)$ may depend on a number of constant parameters (a_l) which characterize the external sources of the force. For a particle in a container of volume V^0 without other external forces, the potential energy U^0 is constant and shall be chosen equal to zero inside V^0 and $+\infty$ outside. In the presence of external forces like static electric or magnetic fields, $U^0 \neq 0$ will be varying inside the container. The parameters (a) determine the strength of the external forces as well as the form and the volume of the container. For constant (a) and varying $\boldsymbol{x}^0$

$$-dU^0 = -\frac{\partial U^0(\boldsymbol{x}^0, a)}{\partial \boldsymbol{x}^0}\, d\boldsymbol{x}^0$$

is equal to the work performed on the particle during a displacement $d\boldsymbol{x}^0$. For fixed values of $\boldsymbol{x}^0$ (and $\boldsymbol{p}^0$), the increase of the potential energy by a change (da_l) of the external parameters is

$$d_{(a)} U^0 = \sum_l \frac{\partial U^0(\boldsymbol{x}^0, a)}{\partial a_l}\, da_l \tag{2.6}$$

which must be interpreted as the work performed on the system by a change of the configuration of the surrounding systems.

For fixed (a), the three equations (2.1) with $i = 1,2,3$ in the system S^0 are the Euler equations of the variational principle

$$\left.\begin{aligned} \delta \int L^0 dt^0 &= 0 \\ L^0 &= -mc^2\sqrt{1 - u^{02}/c^2} - U^0(\boldsymbol{x}^0), \end{aligned}\right\} \tag{2.7}$$

i.e.

$$\frac{d}{dt}\left(\frac{\partial L(\boldsymbol{u}^0, \boldsymbol{x}^0)}{\partial \boldsymbol{u}^0}\right) = \frac{\partial L(\boldsymbol{u}^0, \boldsymbol{x}^0)}{\partial \boldsymbol{x}^0}. \tag{2.8}$$

The canonical momentum $\boldsymbol{P}^0$ corresponding to the Lagrangian (2.7) is

$$\boldsymbol{P}^0 = \frac{\partial L^0(\boldsymbol{u}^0, \boldsymbol{x}^0)}{\partial \boldsymbol{u}^0} = \boldsymbol{p}^0, \tag{2.9}$$

i.e. in S^0 the canonical momentum is identical with the linear momentum $\boldsymbol{p}^0$. The corresponding Hamiltonian

$$\mathfrak{H}^0 = \boldsymbol{P}^0 \cdot \boldsymbol{u}^0 - L^0 = E^0 + U^0(\boldsymbol{x}^0) = c\sqrt{m^2c^2 + p^{02}} + U^0(\boldsymbol{x}^0) \tag{2.10}$$

is equal to the total energy of the particle in the external field. The Hamiltonian equations

$$\frac{d\boldsymbol{p}^0}{dt^0} = -\frac{\partial \mathfrak{H}^0(\boldsymbol{p}^0, \boldsymbol{x}^0)}{\partial \boldsymbol{x}^0}, \quad \frac{d\boldsymbol{x}^0}{dt^0} = \frac{\partial \mathfrak{H}^0(\boldsymbol{p}^0, \boldsymbol{x}^0)}{\partial \boldsymbol{p}^0} \tag{2.11}$$

are equivalent to the equations (2.8) or to (2.1) with $i = 1,2,3$. $\mathfrak{H}^0$ is a constant of the motion

$$\frac{d\mathfrak{H}^0}{dt^0} = -\frac{\partial L^0(\boldsymbol{u}^0, \boldsymbol{x}^0)}{\partial t^0} = 0 \tag{2.12}$$

which is equivalent to the fourth equation (2.1) in S^0. The equation (2.6) may also be written

$$d_{(a)}U^0 = \sum_l \frac{\partial \mathfrak{H}^0(\boldsymbol{p}^0, \boldsymbol{x}^0, a)}{\partial a_l} da_l = d_{(a)}\mathfrak{H}^0. \tag{2.6'}$$

We shall now consider the motion of the particle with respect to an arbitrary system of inertia S. Let $\boldsymbol{v}$ be the velocity of S^0 with respect to S. Then, the corresponding four-velocity V_i is given by (1.3) and for simplicity we shall assume that the connection between the coordinates in S and S^0 is given by a Lorentz transformation without rotation of the spatial axes. If we treat $U^0(\boldsymbol{x}^0)$ as an invariant scalar it may also be regarded as a function of coordinates $x^i = \{\boldsymbol{x}, ct\}$ in S.

$U(x,a)$ then denotes the function obtained from $U^0(\boldsymbol{x}^0, a)$ by eliminating $\boldsymbol{x}^0$ by means of the Lorentz transformation connecting S and S^0, i.e.

$$U(x,a) = U(\boldsymbol{x},t,a) = U^0(\boldsymbol{x}^0,a). \tag{2.13}$$

In the present case, the four-force (2.4) is easily seen to have the form of a 'Lorentz force', i.e.

$$F_i = F_{ik}U^k/c^2 \tag{2.14}$$

where

$$U^i = \left\{ \frac{\boldsymbol{u}}{\sqrt{1 - u^2/c^2}}, \quad \frac{c}{\sqrt{1 - u^2/c^2}} \right\} \tag{2.15}$$

is the four-velocity of the particle, and the antisymmetric tensor F_{ik} is given by

$$F_{ik} = \frac{\partial U(x)}{\partial x^i} V_k - \frac{\partial U(x)}{\partial x^k} V_i. \tag{2.16}$$

Since $F_{ik}U^k$ is a 4-vector, the validity of the expression (2.14) for F_i follows from the remark that it reduces to the expression (2.5) for F_i^0 in the system S^0 where $V_i^0 = -c\delta_{i4}$. Introduction of (2.16) into (2.14) gives

$$F_i = \frac{V_k U^k}{c^2} \frac{\partial U}{\partial x^i} - \frac{V_i}{c^2} \frac{dU}{d\tau}. \tag{2.17}$$

Therefore, if we define a new 4-vector P_i by

$$P_i = p_i + \frac{V_i}{c^2} U(x,a), \tag{2.18}$$

the equations (2.1) may be written

$$\frac{dP_i}{d\tau} = K_i \tag{2.19}$$

with

$$K_i = \frac{V_k U^k}{c^2} \frac{\partial U(x)}{\partial x^i}. \tag{2.20}$$

Since $V^{0i} = c\delta_4^i$, i.e.

$$\frac{\partial U(x)}{\partial x^i} V^i = \frac{\partial U^0(\boldsymbol{x}^0)}{\partial x^{0\varkappa}} V^{0\varkappa} = 0, \tag{2.21}$$

the 4-vector K_i is orthogonal to V^i, i.e.

$$K_i V^i = 0. \tag{2.22}$$

If we put

$$P_i = \{\boldsymbol{P}, -\mathfrak{H}/c\} \tag{2.23}$$

we get from (2.18,3) and (1.3)

$$\left.\begin{aligned} \boldsymbol{P} &= \boldsymbol{p} + \gamma \boldsymbol{v} U(x)/c^2 \\ \mathfrak{H} &= E + \gamma U(x) \end{aligned}\right\} \tag{2.24}$$

Then we get from (1.3), (2.15,20,22)

$$K_i = \left\{ \frac{\mathfrak{K}}{\sqrt{1 - u^2/c^2}}, \; -\frac{(\mathfrak{K} \cdot \boldsymbol{v})/c}{\sqrt{1 - u^2/c^2}} \right\} \tag{2.25}$$

with

$$\mathfrak{K} = -(1 - (\boldsymbol{v} \cdot \boldsymbol{u})/c^2)\gamma \frac{\partial U(\boldsymbol{x},t)}{\partial \boldsymbol{x}}. \tag{2.26}$$

For $i = 1,2,3$ the equations of motion (2.19) are now

$$\frac{d\boldsymbol{P}}{dt} = \mathfrak{K} \tag{2.27}$$

which are the Euler equations of the variational principle

$$\delta \int L dt = 0 \tag{2.28}$$

with the Lagrangian

$$L(\boldsymbol{u},\boldsymbol{x},t) = -mc^2\sqrt{1 - u^2/c^2} - (1 - \boldsymbol{v} \cdot \boldsymbol{u}/c^2)\gamma U(\boldsymbol{x},t). \tag{2.29}$$

For, by differentiating with respect to $\boldsymbol{u}$, we get

$$\frac{\partial L(\boldsymbol{u},\boldsymbol{x},t)}{\partial \boldsymbol{u}} = \boldsymbol{p} + \frac{\boldsymbol{v}}{c^2}\gamma U(\boldsymbol{x},t) = \boldsymbol{P}$$

on account of (2.24), and by differentiation with respect to $\boldsymbol{x}$

$$\frac{\partial L(\boldsymbol{u},\boldsymbol{x}.t)}{\partial \boldsymbol{x}} = -(1 - \boldsymbol{v} \cdot \boldsymbol{u}/c^2)\gamma \frac{\partial U(\boldsymbol{x},t)}{\partial \boldsymbol{x}} = \mathfrak{K} \tag{2.30}$$

on account of (2.26). Thus, $\boldsymbol{P}$ in (2.23) is the canonical momentum and $\mathfrak{K}$ may be called the canonical force. The corresponding Hamiltonian is

$$\left.\begin{aligned}\boldsymbol{P}\cdot\boldsymbol{u} - L &= \boldsymbol{p}\cdot\boldsymbol{u} + (\boldsymbol{v}\cdot\boldsymbol{u})\gamma U(x)/c^2 + mc^2\sqrt{1-u^2/c^2} + (1-\boldsymbol{v}\cdot\boldsymbol{u}/c^2)\gamma U(x)\\ &= E + \gamma U(\boldsymbol{x},t) = \mathfrak{H}.\end{aligned}\right\} \tag{2.31}$$

Hence, the quantity $\mathfrak{H}$ in (2.24) which together with the canonical momentum $\boldsymbol{P}$ defines the 'canonical' four-momentum vector (2.23) is equal to the total energy of the particle in the external field. Therefore, $\gamma U(\boldsymbol{x},t)$ may be interpreted as the potential energy. In contrast to $U^0(\boldsymbol{x}^0)$ and $\mathfrak{H}^0$, both U and $\mathfrak{H}$ are time-dependent and $\mathfrak{H}$ is not a constant of the motion. From (2.19) with $i = 4$ we get, by (2.23,25)

$$\frac{d\mathfrak{H}}{dt} = \mathfrak{K}\cdot\boldsymbol{v} = -(1-\boldsymbol{v}\cdot\boldsymbol{u}/c^2)\gamma\left(\boldsymbol{v}\cdot\frac{\partial U(\boldsymbol{x},t)}{\partial\boldsymbol{x}}\right) = -\frac{\partial L(\boldsymbol{u},\boldsymbol{x},t)}{\partial t} \tag{2.32}$$

on account of (2.21,26,29). The equations (2.27,32) may be comprised in the four-component equation

$$\frac{dP_i}{dt} = \frac{\partial L(\boldsymbol{u},x)}{\partial x^i} = -(1-\boldsymbol{v}\cdot\boldsymbol{u}/c^2)\gamma\frac{\partial U(x)}{\partial x^i} \tag{2.33}$$

on account of (2.30).

If we eliminate the velocity $\boldsymbol{u}$ in (2.31) by means of (2.24), $\mathfrak{H} = \mathfrak{H}(\boldsymbol{P},\boldsymbol{x},t)$ appears as a function of $\boldsymbol{P}$ and $\boldsymbol{x}$ and the equations of motion may be written in the Hamiltonian form

$$\frac{d\boldsymbol{P}}{dt} = -\frac{\partial\mathfrak{H}(\boldsymbol{P},\boldsymbol{x},t)}{\partial\boldsymbol{x}}, \quad \frac{d\boldsymbol{x}}{dt} = \frac{\partial\mathfrak{H}(\boldsymbol{P},\boldsymbol{x},t)}{\partial\boldsymbol{P}}. \tag{2.34}$$

On account of the relation [9]

$$\frac{\sqrt{1-u^2/c^2}}{\sqrt{1-u^{02}/c^2}} = \gamma(1-\boldsymbol{v}\cdot\boldsymbol{u}/c^2) = \frac{1}{\gamma(1+\boldsymbol{v}\cdot\boldsymbol{u}^0/c^2)}, \tag{2.35}$$

the variational principle (2.7,28) is invariant. For, by (2.29,2,7), we get

$$Ldt = \frac{Ld\tau}{\sqrt{1-u^2/c^2}} = \frac{L^0d\tau}{\sqrt{1-u^{02}/c^2}} = L^0dt^0.$$

The preceding considerations are easily generalized to a gas of n non-interacting particles of mass m subjected to the same external force. In this case the Lagrangian L_g is simply the sum of the Lagrangian functions (2.29) for each particle, i.e.

$$\left.\begin{aligned} L_g &= \sum_{r=1}^{n} L^{(r)}(\boldsymbol{u}^{(r)}, \boldsymbol{x}^{(r)}, t) \\ L^{(r)} &= -mc^2\sqrt{1 - u^{(r)2}/c^2} - (1 - \boldsymbol{v}\cdot\boldsymbol{u}^{(r)}/c^2)\gamma U(\boldsymbol{x}^{(r)}, t). \end{aligned}\right\} \tag{2.36}$$

The corresponding Hamiltonian is

$$\mathfrak{H}_g = \sum_{r=1}^{n} \mathfrak{H}^{(r)}(\boldsymbol{P}^{(r)}, \boldsymbol{x}^{(r)}, t). \tag{2.37}$$

The suffix g indicates that the quantity in question refers to the system as a whole. This case is therefore a trivial generalization of the one-body problem and, in the following section, we shall first consider the statistical mechanics of a single particle and afterwards make the generalization to the n-body system. Let P_i^g denote the sum of the canonical four-momenta of all particles in the gas, i.e.

$$P_i^g = \sum_r P_i^{(r)}(\boldsymbol{p}^{(r)}, \boldsymbol{x}^{(r)}, t, a) = \sum_{r=1}^{n} p_i^{(r)} + \frac{V_i}{c^2}\sum_{r=1}^{n} U(\boldsymbol{x}^{(r)}, t, a). \tag{2.38}$$

It depends on the external parameters (a) as well as on the coordinates and momenta. For constant values of the latter quantities an increase (da_l) of the a's changes the quantity P_i^g by an amount

$$d_{(a)} P_i^g = \sum_l \frac{\partial P_i^g}{\partial a_l} da_l = \frac{V_i}{c^2}\sum_{r=1}^{n}\sum_l \frac{\partial U(\boldsymbol{x}^{(r)}, t, a)}{\partial a_l} da_l. \tag{2.39}$$

3. The Structure of Relativistic Phase-spaces

In classical statistical mechanics one introduces the important notion of a 'phase-space' which for a one-particle system is a space of six dimensions where every phase-point corresponds to a definite mechanical state of the system. However, in a relativistic theory it is convenient to introduce a separate phase-space $\Sigma(S)$ for each system of reference S. Each mechanical state is pictured as a point in $\Sigma(S)$ with the six coordinates $(\boldsymbol{P}, \boldsymbol{x})$. The 'state-points' are moving according to the Hamiltonian equations (2.34),

which determine the curve (the phase-track) in $\Sigma(S)$ described by a state-point $(\boldsymbol{P}(t),\boldsymbol{x}(t))$ in the course of the time t.

On account of the Hamiltonian form of the equations of motion in every system S, Liouville's theorem holds in every $\Sigma(S)$ although $\mathfrak{H}$ in general is time dependent. Thus, if $\Omega(t_0)$ is the region in $\Sigma(S)$ which is occupied by state points at the time t_0 and $\Omega(t)$ the region occupied by the same state-points at the time t, then the volumes of the two regions are equal, i. e.

$$\left.\begin{aligned} V_{\Omega(t)} &= \iint\limits_{\Omega(t)} \boldsymbol{dPdx} = \iint\limits_{\Omega(t_0)} \boldsymbol{dPdx} = V_{\Omega(t_0)}; \\ \boldsymbol{dPdx} &= dP_x dP_y dP_z dxdydz. \end{aligned}\right\} \tag{3.1}$$

(In every $\Sigma(S)$ the volume is defined in the same way as in a Euclidean space with Cartesian coordinates).

In S^0 where $\mathfrak{H}^0$ is independent of t^0 the phase-tracks are fixed curves in $\Sigma(S^0)$. This is not the case in S where the direction of a phase-track passing through a fixed point is given by the 'phase velocity' $\left(\frac{d\boldsymbol{P}}{dt}, \frac{d\boldsymbol{x}}{dt}\right)$ which by (2.34) is seen to be time dependent.

Instead of the canonical variables $(\boldsymbol{P}, \boldsymbol{x})$ we may also use the non-canonical variables

$$\xi_\mu = (p_x, p_y, p_z, x, y, z) \tag{3.2}$$

as 'coordinates' of the phase points. From the 'transformation' equations (2.24)

$$\boldsymbol{P} = \boldsymbol{p} + \boldsymbol{v}\gamma U(x)/c^2 \tag{3.3}$$

it is easily seen that the corresponding Jacobian determinant is equal to unity, i. e.

$$J = \frac{d(\boldsymbol{P},\boldsymbol{x})}{d(\boldsymbol{p},\boldsymbol{x})} = 1. \tag{3.4}$$

Thus, by Jacobi's theorem the volume of a region Ω may also be written

$$V_\Omega = \iint\limits_{\Omega} \boldsymbol{dpdx}, \quad \boldsymbol{dpdx} = \prod_{\mu=1}^{6} d\xi_\mu. \tag{3.5}$$

In the new coordinates, Liouville's theorem (3.1) takes the form

$$V_{\Omega(t)} = \iint\limits_{\Omega(t)} \boldsymbol{dpdx} = \iint\limits_{\Omega(t_0)} \boldsymbol{dpdx} = V_{\Omega(t_0)}. \tag{3.6}$$

The equations (3.1,6) show that the volume $V_{\Omega(t)}$ occupied by the state-points which lie inside a region $\Omega(t)$ at time t is independent of t. Further this volume is relativistically invariant in the following sense. Consider the state-points which at the time t^0 in S^0 are situated inside a region $\Omega^0(t^0)$ of $\Sigma(S^0)$. The same state-points are moving through $\Sigma(S)$ of another system S according to the equations (2.34). At the time t their simultaneous positions will span a region $\Omega(t)$. Then

$$V_{\Omega^0(t^0)} = \iint\limits_{\Omega^0(t^0)} \boldsymbol{dp}^0 \boldsymbol{dx}^0 = \iint\limits_{\Omega(t)} \boldsymbol{dp}\boldsymbol{dx} = V_{\Omega(t)} \tag{3.7}$$

independently of the choice of t^0 and t. The proof of this theorem is a little intricate and, for simplicity, we shall consider the special case (which does not spoil the generality of the proof), where Ω^0 and Ω are infinitesimal and the relative velocity $\boldsymbol{v}$ of S and S^0 is

$$\boldsymbol{v} = \{v, 0, 0\}. \tag{3.8}$$

A state-point which at the time t passes through a point $\xi_\mu = (\boldsymbol{p}, \boldsymbol{x})$ in $\Sigma(S)$ will in $\Sigma(S^0)$ go through a point $\xi^0_\mu = (\boldsymbol{p}^0, \boldsymbol{x}^0)$ at a time t^0 given by the Lorentz transformation

$$\left.\begin{aligned} p^0_x &= \gamma[p_x - vE/c^2], \quad p^0_y = p_y, \quad p_z = p^0_z \\ x^0 &= \gamma[x - vt], \qquad\quad y^0 = y, \quad z^0 = z \end{aligned}\right\} \tag{3.9}$$

$$t^0 = \gamma[t - vx/c^2]. \tag{3.10}$$

Here we have made use of the 4-vector character of $p_i = \{\boldsymbol{p}, -E/c\}$. Since $E = c\sqrt{m^2c^2 + p^2}$, the equations (3.9) represent a non-linear transformation

$$\xi^0_\mu = f_\mu(\xi_\nu, t) \tag{3.11}$$

which defines a certain one to one correspondence of the points in $\Sigma(S^0)$ and $\Sigma(S)$. On account of the relation

$$\frac{\partial E}{\partial \boldsymbol{p}} = \frac{c^2 \boldsymbol{p}}{E} = \boldsymbol{u}, \tag{3.12}$$

the partial derivatives $\dfrac{\partial \xi^0_\mu}{\partial \xi_\nu} = \dfrac{\partial f_\mu(\xi, t)}{\partial \xi_\nu}$ are given by the matrix

$$\frac{\partial f_\mu}{\partial \xi_\nu} = \begin{pmatrix} \gamma(1-vu_x/c^2) & -\gamma vu_y/c^2 & -\gamma vu_z/c^2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \tag{3.13}$$

Now, consider the state-points in $\Sigma(S)$ which at the time t are passing through the phase points inside an infinitesimal parallelepiped $\Omega(t)$ spanned by six infitesimal vectors along the 'coordinate axes', i.e.

$$\left.\begin{aligned} d^{(1)}\xi_\mu &= (dp_x, 0, 0, 0, 0, 0) \\ d^{(2)}\xi_\mu &= (0, dp_y, 0, 0, 0, 0) \\ &\cdots\cdots\cdots\cdots \\ &\cdots\cdots\cdots\cdots \\ d^{(6)}\xi_\mu &= (0, 0, 0, 0, 0, dz) \end{aligned}\right\} \tag{3.14}$$

or

$$\left.\begin{aligned} d^{(\alpha)}\xi_\mu &= \delta^\alpha_\mu d\xi_{\alpha)}, \quad \alpha = 1,2,3,4,5,6 \\ &\text{(no summation over } \alpha!) \\ d\xi_\alpha &= (dp_x, dp_y, dp_z, dx, dy, dz). \end{aligned}\right\} \tag{3.15}$$

The volume of this region is given by the determinant

$$dV_{\Omega(t)} = |d^{(\alpha)}\xi_\mu| = |\delta^\alpha_\mu d\xi_{\alpha)}| = \prod_{\alpha=1}^{6} d\xi_\alpha = \boldsymbol{dpdx}. \tag{3.16}$$

In the mapping of $\Sigma(S)$ on $\Sigma(S^0)$, defined by (3.9) or (3.11), the region $\Omega(t)$ corresponds to a region $\Omega^0(t^0, t^0 + dt^0)$ in $\Sigma(S^0)$ which is spanned by the six infinitesimal 'vectors'

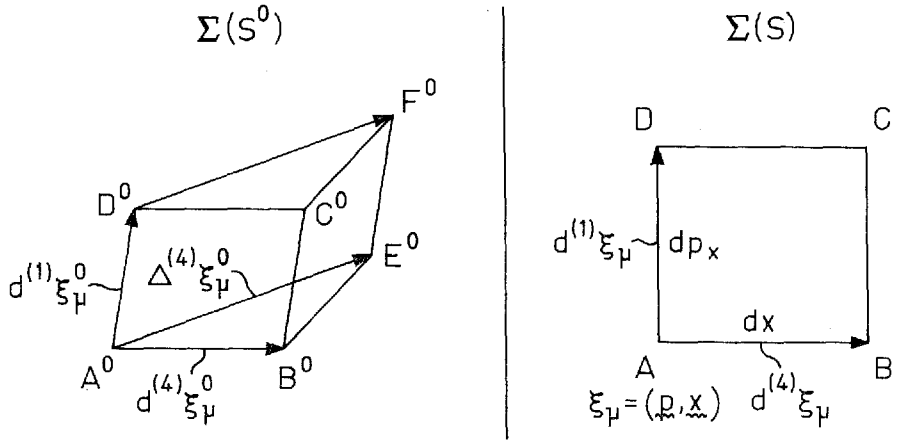
$$d^{(\alpha)}\xi^0_\mu = \sum_\nu \frac{\partial f_\mu(\xi, t)}{\partial \xi_\nu} d^{(\alpha)}\xi_\nu = \frac{\partial f_\mu}{\partial \xi_\alpha} d\xi_{\alpha)}, \tag{3.17}$$

on account of (3.15). The volume of this region is given by the determinant

$$dV_{\Omega^0(t^0, t^0+dt)} = \left|\frac{df_\mu}{\partial \xi_\alpha} d\xi_{\alpha)}\right| = J \prod_{\alpha=1}^{6} d\xi_\alpha = J dV_{\Omega(t)} \tag{3.18}$$

where the Jacobian J is the determinant of the matrix (3.13), i.e.

$$J = \frac{d(\boldsymbol{p}^0, \boldsymbol{x}^0)}{d(\boldsymbol{p}, \boldsymbol{x})} = \gamma^2(1 - vu_x/c^2). \tag{3.19}$$



In the 2-dimensional picture above the region $\Omega(t)$ in $\Sigma(S)$ is represented by the inside of the rectangle $ABCD$ with sides dx and dp_x, the vectors $d^{(1)}\xi_\mu$ and $d^{(4)}\xi_\mu$ being represented by the lines $\overrightarrow{AD}$ and $\overrightarrow{AB}$, respectively. The corresponding vectors $d^{(1)}\xi^0_\mu$ and $d^{(4)}\xi^0_\mu$ in $\Sigma(S^0)$, as given by (3.17), are represented by the lines $\overrightarrow{A^0D^0}$ and $\overrightarrow{A^0B^0}$, and the region $\Omega^0(t^0, t^0+dt^0)$ is the inside of the parallelogram $A^0B^0C^0D^0$.

According to (3.18,19) the volume $dV_{\Omega^0(t^0,\,t^0+dt^0)}$ of this region is *not* equal to the volume $dV_{\Omega(t)}$ of $\Omega(t)$. However, the points inside $\Omega^0(t^0, t^0+dt^0)$ are *not* the positions in $\Sigma(S^0)$ of the state points in $\Omega(t)$ at the same time t^0, since the passage time, for the points along the lines parallel to A^0B^0, according to (3.10) vary linearly from t^0 to t^0+dt^0 with

$$dt^0 = -\frac{\gamma v}{c^2}\,dx \tag{3.20}$$

which is negative. During the time $|dt^0| = \frac{\gamma v}{c^2}\,dx$, the points on the line B^0C^0 are displaced by a displacement vector $\delta\xi^0_\mu$ which, if we neglect small terms of the second order, is given by

$$d\xi^0_\mu = \left(\frac{d\boldsymbol{p}^0}{dt^0}\,|dt^0|,\ \frac{d\boldsymbol{x}^0}{dt^0}\,|dt^0|\right) = \left(-\frac{\partial\mathfrak{H}^0}{\partial\boldsymbol{x}^0}\,\frac{\gamma v dx}{c^2},\ \frac{\gamma v\boldsymbol{u}^0}{c^2}\,dx\right). \tag{3.21}$$

In the picture this constant vector is represented by $\overrightarrow{B^0E^0}$ or $\overrightarrow{C^0F^0}$. The state-points, which at the time $t^0+dt^0 = t^0 - \frac{\gamma}{c^2}\,dx$ were in B^0 and C^0, will

at the time t^0 be in the positions E^0 and F^0, respectively, and the whole line B^0C^0 will be displaced to E^0F^0. Thus, the region $\Omega^0(t^0)$ which at the time t^0 is occupied by the state points inside $\Omega(t)$ is in the figure above represented by the parallelogram $A^0E^0F^0D^0$ spanned by the vectors $\overrightarrow{A^0D^0}$ and $\overrightarrow{A^0E^0}$, i.e. by the vectors $d^{(1)}\xi^0_\mu$ and $d^{(4)}\xi^0_\mu + \delta\xi^0_\mu = \Delta\xi^0_\mu$. Therefore, in the 6-dimensional phase space the region $\Omega^0(t^0)$ is spanned by the six vectors

$$\Delta^{(\alpha)}\xi^0_\mu = \{d^{(1)}\xi^0_\mu, d^{(2)}\xi^0_\mu, d^{(3)}\xi^0_\mu, \Delta\xi^0_\mu, d^{(5)}\xi^0_\mu, d^{(6)}\xi^0_\mu\} \tag{3.22}$$

with

$$\left.\begin{aligned} \Delta^{(4)}\xi^0_\mu &= \Delta\xi^0_\mu = d^{(4)}\xi^0_\mu + \delta\xi^0_\mu = \frac{\partial f\mu}{\partial\xi_4}dx + \delta\xi^0_\mu \\ &= \left(-\frac{\partial\mathfrak{H}^0}{\partial x^0}\frac{\gamma v}{c^2},\ -\frac{\partial\mathfrak{H}^0}{\partial y^0}\frac{\gamma v}{c^2},\ -\frac{\partial\mathfrak{H}^0}{\partial z^0}\frac{\gamma v}{c^2},\ \gamma\left(1+\frac{vu^0_x}{c^2}\right),\ \frac{\gamma v u^0_y}{c^2},\ \frac{\gamma v u^0_z}{c^2}\right)dx \end{aligned}\right\} \tag{3.23}$$

on account of (3.17,21,13). The other vectors $\Delta^{(\alpha)}\xi^0_\mu$ are given by (3.17,13) The volume of the region spanned by the vectors (3.22) is

$$dV_{\Omega^0(t^0)} = |\Delta^{(\alpha)}\xi_\mu|$$

for which one easily gets the value

$$dV_{\Omega^0(t^0)} = \gamma^2(1 - vu_x/c^2)(1 + vu^0_x/c^2)\boldsymbol{dpdx}$$

or, on account of (2.35) and (3.8,16),

$$dV_{\Omega^0(t^0)} = \boldsymbol{dpdx} = dV_{\Omega(t)}. \tag{3.24}$$

Since dV_Ω is invariant under arbitrary spatial rotations, it is obvious that (3.24) holds for an arbitrary system S (arbitrary $\boldsymbol{v}$). Thus, for two arbitrary Lorentz systems S and S' we have

$$dV_{\Omega(t)} = dV_{\Omega'(t')}. \tag{3.25}$$

The generalization of these results to a system of n non-interacting particles is trivial. The phase spaces $\Sigma(S)$ are $6n$-dimensional, and as the coordinates of the phase-points we may take the $6n$ variables

$$\xi_\mu = (\boldsymbol{p}^{(1)}, \boldsymbol{x}^{(1)}, \ldots, \boldsymbol{p}^{(n)}, \boldsymbol{x}^{(n)}, \ldots \boldsymbol{p}^{(n)}, \boldsymbol{x}^{(n)}). \tag{3.26}$$

If the volume of a region Ω in $\Sigma(S)$ is defined by

$$V_\Omega = \int_\Omega \cdot\cdot \int \prod_{\mu=1}^{6n} d\xi_\mu = \int_\Omega \cdot\cdot \int \boldsymbol{dp}^{(1)}\boldsymbol{dx}^{(1)} \ldots . \boldsymbol{dp}^{(n)}\boldsymbol{dx}^{(n)} \tag{3.27}$$

it is obvious that Liouville's theorem (3.6) as well as the relativistic invariance of dV_Ω, i.e. equation (3.24) holds also for a gas of n particles.

4. Statistical Ensembles of Mechanical Systems in the Phase-Space $\Sigma(S)$ of an Arbitrary Lorentz System S. Canonical Ensembles

Let us start by considering an arbitrary ensemble of one-particle systems. In $\Sigma(S)$ the distribution of the state-points of the ensemble is described by a probability density $\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)$ which in general depends explicitly on the time. The number of systems which at the time t are lying inside an infinitesimal region $\Omega(t)$ of volume $dV_{\Omega(t)}$ at the place $(\boldsymbol{p},\boldsymbol{x})$ is then by definition

$$N\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)dV_{\Omega(t)}, \tag{4.1}$$

where N is the total number of systems in the ensemble ($N \to \infty$). At a different time t_0 the same number of state-points is given by

$$N\mathfrak{P}(\boldsymbol{p}_0,\boldsymbol{x}_0,t_0)dV_{\Omega(t_0)} \tag{4.2}$$

where

$$dV_{\Omega(t_0)} = dV_{\Omega(t)} \tag{4.3}$$

on account of (3.6). Thus, (4.1,2) gives

$$\mathfrak{P}(\boldsymbol{p}_0,\boldsymbol{x}_0,t_0) = \mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t) \tag{4.4}$$

which shows that $\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)$ is a constant of the motion, i.e.

$$\frac{d\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)}{dt} = \frac{\partial\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)}{\partial\boldsymbol{x}}\cdot\boldsymbol{u} + \frac{\partial\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)}{\partial\boldsymbol{p}}\cdot\frac{d\boldsymbol{p}}{dt} + \frac{\partial\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)}{\partial t} = 0. \tag{4.5}$$

By integration over the whole phase-space we get for all t

$$\iint \mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)\boldsymbol{dpdx} = 1. \tag{4.6}$$

All these relations hold for any Lorentz system. In the phase-space $\Sigma(S')$ of another system S', the state-points given by (4.1) occupy at a time t' an infinitesimal region $\Omega'(t')$ around the point $(\boldsymbol{p}',\boldsymbol{x}')$, where $(\boldsymbol{p}'\boldsymbol{x}',t')$ and

$(\boldsymbol{p},\boldsymbol{x},t)$ are connected by the Lorentz transformation leading from S to S'. On account of (3.25) the volume $dV_{\Omega'(t')}$ of this region is equal to $dV_{\Omega(t)}$. Therefore, since the number (4.1) of systems is also equal to

$$N\mathfrak{P}'(\boldsymbol{p}',\boldsymbol{x}',t')dV_{\Omega'(t')}, \tag{4.7}$$

where $\mathfrak{P}'(\boldsymbol{p}',\boldsymbol{x}',t')$ is the probability density in $\Sigma(S')$, we may conclude that the probability density is a relativistic invariant, i.e.

$$\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t) = \mathfrak{P}'(\boldsymbol{p}',\boldsymbol{x}',t') \tag{4.8}$$

where the arguments in the two functions are connected by the Lorentz transformation $S \to S'$.

The mean value of any physical quantity $F(\boldsymbol{p},\boldsymbol{x},t)$ like the energy $\mathfrak{H}$ or the canonical momentum $\boldsymbol{P}$ is, at the time t, given by

$$\langle F(\boldsymbol{p},\boldsymbol{x},t)\rangle = \iint F(\boldsymbol{p},\boldsymbol{x},t)\mathfrak{P}(\boldsymbol{p},\boldsymbol{x},t)d\boldsymbol{p}d\boldsymbol{x}. \tag{4.9}$$

For a system of n non-interacting particles, the probability density $\mathfrak{P}_g(\xi_\mu,t)$ in the 6 n-dimensional phase-space $\Sigma(S)$ is the product of the probability densities in the 6-dimensional phase-spaces of the separate particles

$$\mathfrak{P}_g(\xi_\mu,t) = \prod_{r=1}^{n} \mathfrak{P}^{(r)}(\boldsymbol{p}^{(r)},\boldsymbol{x}^{(r)},t). \tag{4.10}$$

We shall now in particular consider the case where the ensemble is canonically distributed in S^0. Such an ensemble represents an adequate description of our knowledge about the mechanical state of a gas in a container at rest in S^0 and in thermal equilibrium with a heat reservoir of given temperature T^0. For an ideal gas each of the particles in the gas will then be canonically distributed with a probability density

$$\mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0) = e^{(\varphi^0-\theta^0\mathfrak{H}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,a))/k} \tag{4.11}$$

where k is Boltzmann's constant and $\theta^0 = 1/T^0$ is the reciprocal of the proper temperature T^0.

$$\varphi^0 = \varphi_p^0 + \varphi_q^0 \tag{4.12}$$

are phase-independent quantities defined by

$$\left.\begin{aligned} e^{-\varphi^0/k} &= \iint e^{-\theta^0\mathfrak{H}^0/k}d\boldsymbol{p}^0d\boldsymbol{x}^0, \\ e^{-\varphi_p^0/k} = \int e^{-\theta^0E^0/k}d\boldsymbol{p}^0, &\quad e^{-\varphi_q^0/k} = \int e^{-\theta^0U^0(\boldsymbol{x}^0,a)/k}d\boldsymbol{x}^0. \end{aligned}\right\} \tag{4.13}$$

These equations determine $\varphi^0 = \varphi^0(\theta^0, a)$ as a function of θ^0 and the external parameters (a) which define the thermodynamical state of the system in S^0. The thermodynamical significance of φ^0 is given by the relation

$$F^0 = n\varphi^0/\theta^0 = \Phi^0/\theta^0 \tag{4.14}$$

where F^0 is the free energy of the gas in the rest System S^0 (see § 5).

While $\mathfrak{P}^0$ in S^0 is independent of t^0 the probability density $\mathfrak{P}$ in S is time dependent. Since the canonical four-momentum P_i is a 4-vector we have

$$P_i V^i = P_i^0 V^{0i} = -\mathfrak{H}^0. \tag{4.15}$$

Thus, if we introduce the 4-vector (1.15,16)

$$\theta^i = \theta^0 V^i = \theta V^i \tag{4.16}$$

we get, on account of the invariance of the probability density expressed by (4.8) with $S' = S^0$,

$$\mathfrak{P}(\boldsymbol{p}, \boldsymbol{x}, t) = e^{(\varphi + \theta^i P_i)/k}, \tag{4.17}$$

where

$$\varphi = \varphi^0 \tag{4.18}$$

is an invariant.

In the general system S the thermodynamical state is determined by the four parameters θ^i together with the external parameters (a_l). The expression (4.17) is closely related to expressions used by Mazur and Lurçat and by Barut [10].

5. The Mean Values of the Energy and the Canonical Momentum and their Transformation Properties

The mean values in question are, in a system S,

$$\left.\begin{aligned} \langle \mathfrak{H} \rangle &= \iint \mathfrak{H}(\boldsymbol{p}, \boldsymbol{x}, t)\mathfrak{P}(\boldsymbol{p}, \boldsymbol{x}, t)\boldsymbol{dpdx}, \\ \langle \boldsymbol{P} \rangle &= \iint \boldsymbol{P}(\boldsymbol{p}, \boldsymbol{x}, t)\mathfrak{P}(\boldsymbol{p}, \boldsymbol{x}, t)\boldsymbol{dpdx}, \end{aligned}\right\} \tag{5.1}$$

where the integrations are to be performed at constant time. From these expressions it would seem that $\langle \mathfrak{H} \rangle$ and $\langle \boldsymbol{P} \rangle$ are time dependent. However,

a calculation of the integrals (5.1) will show that these quantities are independent of t for a canonical ensemble with $\mathfrak{P}$ given by (4.17).

Let us again for simplicity arrange it so that the velocity of S^0 with respect to S is

$$\boldsymbol{v} = \{v,0,0\} \tag{5.2}$$

in which case the equations (3.9) are valid. In order to perform the integrations in (5.1) it is convenient for constant t to introduce the quantities $\boldsymbol{p}^0, \boldsymbol{x}^0$ defined by (3.9) as new variables of integration. The inverse transformations of (3.9) are (for constant t)

$$\left.\begin{aligned} p_x &= \gamma[p_x^0 + vE^0/c^2], \quad p_y = p_y^0, \quad p_z = p_z^0 \\ x &= vt + x^0/\gamma, \qquad\quad y = y^0, \quad z = z^0. \end{aligned}\right\} \tag{5.3}$$

According to Jacobi's theorem we have then to replace $\boldsymbol{dp}\,\boldsymbol{dx}$ by

$$\boldsymbol{dpdx} = J\boldsymbol{dp}^0\boldsymbol{dx}^0. \tag{5.4}$$

Here J is the Jacobian determinant corresponding to (5.3) which is easily seen to be

$$J = \frac{d(\boldsymbol{p},\boldsymbol{x})}{d(\boldsymbol{p}^0,\boldsymbol{x}^0)} = 1 + vu_x^0/c^2 = 1 + vp_x^0/E^0. \tag{5.5}$$

J in (5.5) is of course the reciprocal of the determinant (3.19) (comp. (2.35)). Since P_i is a 4-vector and $\boldsymbol{P}^0 = \boldsymbol{p}^0$ we have

$$\mathfrak{H} = \gamma[\mathfrak{H}^0 + vp_x^0]$$

and, because of the invariance of the probability density, the first integral in (5.1) becomes

$$\langle\mathfrak{H}\rangle = \iint \mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0)\gamma(\mathfrak{H}^0 + vp_x^0)(1 + vp_x^0/E^0)\boldsymbol{dp}^0\boldsymbol{dx}^0. \tag{5.6}$$

Here we have made use of the time independence of $\mathfrak{P}^0$.

In the next section we shall consider a case where the probability density $\mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,t^0)$ is t^0-dependent. In applying the formula (5.6) one has then in $\mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,t^0)$ for the argument t^0 to substitute the expression (3.10), which by means of (5.3) may be written

$$t^0 = \gamma[t - vx/c^2] = t/\gamma - vx^0/c^2. \tag{5.7}$$

However, in the present case we get from (5.6)

$$\langle \mathfrak{H} \rangle = \gamma \left[\langle \mathfrak{H}^0 \rangle^0 + v \langle p_x^0 \rangle^0 + \langle \frac{v \mathfrak{H}^0}{E^0} p_x^0 \rangle^0 + \langle \frac{v^2 p_x^{02}}{E^0} \rangle^0 \right], \tag{5.8}$$

where $\langle\ \rangle^0$ denotes the mean value over the ensemble (4.11) in $\Sigma(S^0)$. Since $\mathfrak{H}^0 = c\sqrt{m^2c^2 + p^{02}} + U^0(\boldsymbol{x}^0)$ and E^0 depend on the squares of p_x^0, p_y^0 and p_z^0 only and the integration over these variables goes from $-\infty$ to $+\infty$, where $\mathfrak{H}^0 = +\infty$ and $\mathfrak{P}^0 = 0$, it is obvious that

$$\left.\begin{aligned} \langle p_x^0 \rangle^0 &= \langle p_y^0 \rangle^0 = \langle p_z^0 \rangle^0 = 0 \\ \langle p_x^0 p_y^0 \rangle^0 &= \langle p_x^0 p_z^0 \rangle^0 = \langle \frac{\mathfrak{H}^0 p_x^0}{E^0} \rangle^0 = 0. \end{aligned}\right\} \tag{5.9}$$

Further, as

$$\frac{c^2 p_x^{02}}{E^0} = p_x^0 \frac{\partial E^0}{\partial p_x^0} = p_x^0 \frac{\partial \mathfrak{H}^0}{\partial p_x^0}, \tag{5.10}$$

we get by partial integration

$$\left.\begin{aligned} \langle \frac{c^2 p_x^{02}}{E^0} \rangle^0 &= \int\int p_x^0 \frac{\partial \mathfrak{H}^0}{\partial p_x^0} e^{(\varphi^0 - \theta^0 \mathfrak{H}^0)/k} \boldsymbol{dp}^0 \boldsymbol{dx}^0 \\ &= -\frac{k}{\theta^0} \int\int p_x^0 \frac{\partial \mathfrak{P}^0}{\partial p_x^0} \boldsymbol{dp}^0 \boldsymbol{dx}^0 = kT^0 \int\int \mathfrak{P}^0 \boldsymbol{dp}^0 \boldsymbol{dx}^0 = kT^0. \end{aligned}\right\} \tag{5.11}$$

Hence,

$$\langle \mathfrak{H} \rangle = \gamma \left[\langle \mathfrak{H}^0 \rangle^0 + \frac{v^2}{c^2} kT^0 \right]. \tag{5.12}$$

Similarly we get from the second equation (5.1), remembering that

$$P_x = \gamma [p_x^0 + v \mathfrak{H}^0 / c^2], \quad P_y = P_y^0, \quad P_z = P_z^0, \tag{5.13}$$

$$\left.\begin{aligned} \langle P_x \rangle &= [\langle \mathfrak{H}^0 \rangle^0 + kT^0] \gamma v / c^2 \\ \langle P_y \rangle &= \langle P_z \rangle = 0 \end{aligned}\right\} \tag{5.14}$$

on account of (5.9,11).

For a gas of n non-interacting particles, the equations (5.12,14) hold for each particle separately and, by multiplying these equations by n, we get the corresponding formulae for the mean values of the total energy and canonical momentum of the gas. Thermodynamically, these quantities are to be identified with the energy and momentum of the gas, i. e.

$$\left.\begin{aligned} H &= \langle \mathfrak{H}_g \rangle = n\langle \mathfrak{H} \rangle, \quad H^0 = \langle \mathfrak{H}_g^0 \rangle^0 = n\langle \mathfrak{H}^0 \rangle^0 \\ \boldsymbol{G} &= \langle \boldsymbol{P}_g \rangle = n\langle \boldsymbol{P} \rangle, \quad \boldsymbol{G}^0 = \langle \boldsymbol{P}_g^0 \rangle^0 = n\langle \boldsymbol{P}^0 \rangle^0 \\ G_i &= \langle P_i^g \rangle = n\langle P_i \rangle, \quad G_i^0 = \langle P_i^{g0} \rangle^0 = n\langle P_i^0 \rangle^0. \end{aligned}\right\} \quad (5.15)$$

The justification for this identification lies in the fact that the fluctuations of these quantities normally are completely negligible for large n of the order of the number of particles in a ponderable amount of gas. It is perhaps a little surprising that $\boldsymbol{G}$ is identified with the mean value of the *canonical* momentum and not with that of the linear momentum. However, it should be noted that the potential $U^0(\boldsymbol{x}^0)$ of a particle in S^0 will represent a momentum $\gamma v\langle U^0\rangle^0/c^2$ in S and, according to (2.24), this is just the difference between the mean values of the canonical and the linear momenta. In the case where there are no other external fields than the forces from the walls, $\langle U^0\rangle^0$ is zero and there is then no difference between $\langle \boldsymbol{P}\rangle$ and $\langle \boldsymbol{p}\rangle$.

From (5.12,14,15) we now get for the momentum and energy of the gas

$$\left.\begin{aligned} \boldsymbol{G} &= [H^0 + nkT^0]\gamma \boldsymbol{v}/c^2 \\ H &= \left[H^0 + \frac{v^2}{c^2} nkT^0\right]\gamma \end{aligned}\right\} \quad (5.16)$$

holding for any direction of v. This may also be written

$$\left.\begin{aligned} G_i &= \frac{H^0}{c^2} V_i + g_i \\ g_i &= \left\{\frac{nkT^0}{c^2}\gamma \boldsymbol{v}, \; -\frac{nkT^0}{c^2}\frac{v^2\gamma}{c}\right\}. \end{aligned}\right\} \quad (5.17)$$

The quantity g_i (and hence G_i) is *not* a 4-vector, but it satisfies in any system S the relation

$$\left.\begin{aligned} g_i V^i &= 0, \\ G_i V^i &= -H^0. \end{aligned}\right\} \quad (5.18)$$

i.e.

Since F_i is a 4-vector we have, in the case (5.2), the following transformation formula for the mechanical force $\mathfrak{F}$ and the rate of mechanical work $\mathfrak{F}\boldsymbol{u}$:

$$\left.\begin{aligned}
\mathfrak{F}_x &= \frac{\mathfrak{F}_x^0 + v(\mathfrak{F}^0 \cdot \boldsymbol{u}^0)/c^2}{1 + vu_x^0/c^2}, \quad \mathfrak{F}_y = \frac{\mathfrak{F}_y^0}{\gamma[1 + vu_x^0/c^2]} \\
\mathfrak{F}_z &= \frac{\mathfrak{F}_z^0}{\gamma[1 + vu_x^0/c^2]}, \qquad \mathfrak{F}^0 = -\frac{\partial U^0(\boldsymbol{x}^0)}{\partial \boldsymbol{x}^0} \\
\mathfrak{F} \cdot \boldsymbol{u} &= \frac{\mathfrak{F}^0 \cdot \boldsymbol{u}^0 + v\mathfrak{F}_x^0}{1 + vu_x^0/c^2}.
\end{aligned}\right\} \tag{5.19}$$

Similarly, we get for the canonical force (2.25,26)

$$\left.\begin{aligned}
\mathfrak{K}_x &= \frac{\mathfrak{K}_x^0}{1 + vu_x^0/c^2}, \quad \mathfrak{K}_y = \frac{\mathfrak{K}_y^0}{\gamma[1 + vu_x^0/c^2]} \\
\mathfrak{K}_z &= \frac{\mathfrak{K}_z^0}{\gamma[1 + vu_x^0/c^2]}, \quad \mathfrak{K}^0 = -\frac{\partial U^0(\boldsymbol{x}^0)}{\partial \boldsymbol{x}^0} \\
\mathfrak{K} \cdot \boldsymbol{v} &= \frac{\mathfrak{K}^0 \cdot \boldsymbol{v}}{1 + vu_x^0/c^2} = \frac{\mathfrak{K}_x^0 v}{1 + vu_x^0/c^2}.
\end{aligned}\right\} \tag{5.20}$$

The mean value of $\mathfrak{F}^0 = \mathfrak{K}^0$ over the ensemble (4.11) is

$$\left.\begin{aligned}
\langle \mathfrak{F}^0 \rangle^0 = \langle \mathfrak{K}^0 \rangle^0 &= -\int\int \frac{\partial U^0(\boldsymbol{x}^0)}{\partial \boldsymbol{x}^0} e^{(\varphi^0 - \theta^0 E^0 - \theta^0 U^0)/k} \boldsymbol{dp}^0 \boldsymbol{dx}^0 \\
&= \frac{k}{\theta^0} \int\int \frac{\partial}{\partial \boldsymbol{x}^0} (e^{(\varphi^0 - \theta^0 E^0 - \theta^0 U^0)/k}) \boldsymbol{dp}^0 \boldsymbol{dx}^0 = 0
\end{aligned}\right\} \tag{5.21}$$

since $\mathfrak{P}^0$ vanishes outside the container. Similarly, we find

$$\langle \mathfrak{F}^0 \cdot \boldsymbol{u}^0 \rangle^0 = \langle \mathfrak{K}^0 \cdot \boldsymbol{v} \rangle^0 = 0. \tag{5.22}$$

By means of Jacobi's theorem and (5.4,5,19,20) we get, therefore, for the mean values of the forces and the rates of work in the system S

$$\left.\begin{aligned}
\langle \mathfrak{F} \rangle &= \langle \mathfrak{K} \rangle = 0 \\
\langle \mathfrak{F} \cdot \boldsymbol{u} \rangle &= \langle \mathfrak{K} \cdot \boldsymbol{v} \rangle = 0.
\end{aligned}\right\} \tag{5.23}$$

Although the mean value of the total external force acting on the system is zero in a canonical ensemble, as one should expect for a thermodynamical system at rest and in thermal equilibrium in S^0, we get of course in general a non-zero result if we take the mean value over this quantity when the

position of the particle is fixed or confined to a finite region ω^0 in space. Then we get in S^0, instead of (5.21),

$$\left.\begin{aligned}\langle\mathfrak{F}^0\rangle^0_{\omega^0} = \langle\mathfrak{K}^0\rangle^0_{\omega^0} &= \int e^{(\varphi^0-\theta^0E^0)/k}\boldsymbol{dp}^0kT^0\int_{\omega^0}\frac{\partial e^{-\theta^0U^0(\boldsymbol{x}^0)/k}}{\partial\boldsymbol{x}^0}\boldsymbol{dx}^0\\ &= kT^0\int_{\sigma^0}e^{-\theta^0U^0(\boldsymbol{x}^0)/k}\boldsymbol{n}d\sigma^0\Big/\int e^{-\theta^0U^0(\boldsymbol{x}^0)/k}\boldsymbol{dx}^0,\end{aligned}\right\}\quad(5.24)$$

where the integral in the numerator is taken over the surface σ^0 of ω^0 and $\boldsymbol{n}$ is an outward normal to the surface element $d\sigma$. The volume integral in the denominator in (5.24) follows from (4.13). In the case where the forces from the walls of the container are the only external forces present, we have

$$U^0(\boldsymbol{x}^0) = \left\{\begin{matrix}0 & \text{inside the container}\\ +\infty & \text{outside the container}\end{matrix}\right\}\quad(5.25)$$

and the denominator becomes

$$\int e^{-\theta^0U^0/k}\boldsymbol{dx}^0 = \mathfrak{V}^0\quad(5.26)$$

where $\mathfrak{V}^0$ is the rest volume of the container.

Now let us for ω^0 take a small cylinder with end surfaces $d\sigma_1^0$ and $d\sigma_2^0$ lying immediately inside and outside the container wall, respectively. (Actually we have to think of the wall as consisting of a thin transition layer inside which the potential rises rapidly but continuously from the value 0 at $d\sigma_1^0$ to a very large value at $d\sigma_2^0$.) Then, we get from (5.24) in the case (5.25)

$$\langle\mathfrak{F}^0\rangle^0_{\omega^0} = \langle\mathfrak{K}^0\rangle^0_{\omega^0} = kT^0d\sigma_1^0\boldsymbol{n}_1/\mathfrak{V}^0\quad(5.27)$$

where n_1 is the inward normal of the container wall. When multiplied by the number n of particles and divided by $d\sigma_1^0$ (5.27) gives the normal pressure $\mathfrak{p}^0$ of the wall on the gas. Hence,

$$\mathfrak{p}^0 = nkT^0/\mathfrak{V}^0.\quad(5.28)$$

When U^0 is given by (5.25) the pressure is the same everywhere, the thermodynamical body is homogeneous. On the other hand, when $U^0(\boldsymbol{x}^0) \neq 0$ inside he container, the pressure varies as $e^{-\theta^0U_1^0/k}$, where U_1^0 is the value of the

potential U^0 at the place considered. If the considerations leading to (5.24,27) are carried through in the system S one easily finds by means of (5.19) that the pressure is an invariant, i.e.

$$\mathfrak{p} = \mathfrak{p}^0. \tag{5.29}$$

In the homogeneous case (5.25) where (5.28) holds the equations (5.16) may also be written

$$\left.\begin{aligned} \boldsymbol{G} &= [H^0 + \mathfrak{p}^0\mathfrak{V}^0]\gamma\boldsymbol{v}/c^2 \\ H &= \left[H^0 + \frac{v^2}{c^2}\mathfrak{p}^0\mathfrak{V}^0\right]\gamma \end{aligned}\right\} \tag{5.30}$$

which are the equations for a thermodynamical fluid from which we started our considerations in reference 4.

Finally we shall consider the statistical analogue of the thermodynamical entropy S. If we put

$$\mathfrak{P} = e^{\eta}, \quad \mathfrak{P}^0 = e^{\eta^0}, \tag{5.31}$$

then the invariance of the probability density entails the invariance of the 'probability exponential' η, i.e.

$$\eta(\boldsymbol{p},\boldsymbol{x},t) = \eta^0(\boldsymbol{p}^0,\boldsymbol{x}^0) \tag{5.32}$$

where the arguments in these functions are connected by the equations (5.3). Hence

$$\langle\eta\rangle = \langle\eta^0\rangle^0. \tag{5.33}$$

This also follows by means of Jacobi's theorem and (5.4,5) which gives

$$\begin{aligned} \langle\eta\rangle &= \iint \eta\mathfrak{P}\boldsymbol{dpdx} = \iint \eta^0\mathfrak{P}^0(1 + vp_x^0/E^0)\boldsymbol{dp}^0\boldsymbol{dx}^0 \\ &= \langle\eta^0\rangle^0 + v\langle\eta^0 p_x^0/E^0\rangle^0. \end{aligned}$$

By the arguments leading to (5.9) it follows that the last term in this expression is zero so that (5.33) follows. (5.33) holds for every particle and from (4.10) we get for the mean value of the probability exponential for a gas of n particles

$$\left.\begin{aligned} \eta_g &= \ln\mathfrak{P}_g \\ \langle\eta_g\rangle &= n\langle\eta\rangle = n\langle\eta^0\rangle^0 = \langle\eta_g^0\rangle^0. \end{aligned}\right\} \tag{5.34}$$

According to classical statistical mechanics the entropy S^0 of the gas in the rest system is

$$S^0 = -k\langle\eta_g^0\rangle^0 = -kn\langle\eta^0\rangle^0 \tag{5.35}$$

and, since the entropy is a relativistic invariant, (5.34) shows that the entropy S in an arbitrary system of inertia must be given by

$$S = -k\langle\eta_g\rangle = -kn\langle\eta\rangle. \tag{5.36}$$

For a canonical ensemble (4.17),

$$\eta = \ln\mathfrak{P} = (\varphi + \theta^i P_i)/k.$$

Hence

$$S = -n\varphi - n\theta^i\langle P_i\rangle \tag{5.37}$$

or, by (5.15),

$$\left.\begin{aligned} \Phi &= -\theta^i G_i - S \\ \Phi &= n\varphi. \end{aligned}\right\} \tag{5.38}$$

Although G_i is not a 4-vector, $\theta^i G_i$ is an invariant. For we have, by (5.18) and (4.16),

$$\theta^i G_i = -\theta^0 H^0 = -H^0/T^0. \tag{5.39}$$

On account of the invariance of the entropy, (5.38) may then be written

$$\left.\Phi = \Phi^0 = \frac{H^0 - T^0 S^0}{T^0} = F^0/T^0\right\} \tag{5.40}$$

in accordance with (4.14).

In the present section we have considered the statistical expressions for the thermodynamic state functions G_i, p and S which are functions of θ^i and (a). The change of these quantities in a process connecting two equilibrium states of the body is obtained by simple differentiation. However, we shall also consider quantities like $\Delta\boldsymbol{I}$ and ΔA (the mechanical impulse and the work) that are not absolute differentials and which therefore depend on the character of the process. In the next section we shall in particular consider processes which are reversible.

6. Statistical Description of a Reversible Process. The Mechanical Impulse and Work. The Four-Momentum of Supplied Heat

Consider a reversible thermodynamical process connecting to equilibrium states (θ^i, a_l) and $(\theta^i + \Delta\theta^i, a_l + da_l)$ and let us for the moment assume *that the rest system S^0 is fixed during the process*, which means that the velocity

$\boldsymbol{v}$ of the thermodynamical body with respect to S is constant. Then, the change of θ^i is due solely to a change in the temperature T^0 of the amount ΔT^0. Now, a process is reversible if it is performed so slowly that the system may be considered going through a succession of equilibrium states with temperatures $T^0(t^0)$ and external parameters $a_l(t^0)$, which are 'infinitely' slowly varying monotonic functions of the time t^0. If τ^0 is the duration of the process we may assume that the temperature and the external parameters rise from the initial values (T^0, a_l) to the final values $(T^0 + \Delta T^0, a_l + \Delta a_l)$ in the time interval

$$0 \leq t^0 \leq \tau^0. \tag{6.1}$$

Experimentally, the body has during the process to be brought into contact with a 'continuous' succession of heat reservoirs of temperatures $T^0(t^0)$.

From classical statistical mechanics we know that the adequate statistical description of this process in the system S^0 is furnished by a 'quasi-canonical' ensemble with a probability density (for each particle) of the type

$$\mathfrak{P}^0(\boldsymbol{p}^0, \boldsymbol{x}^0, \theta^0(t^0), a(t^0)) = \exp\{(\varphi^0(\theta^0, a) - \theta^0(t^0)\mathfrak{H}^0(\boldsymbol{p}^0, \boldsymbol{x}^0, a(t^0))/k\}. \tag{6.2}$$

Like $T^0(t^0)$ and $a(t^0)$,

$$\theta^0(t^0) = 1/T^0(t^0) \tag{6.3}$$

is also a slowly varying function in the interval (6.1) but constant outside, i.e.

$$\theta^0(t^0) = \left\{ \begin{array}{ll} \theta^0 & \text{for } t^0 \leqslant 0 \\ \theta^0 + \Delta\theta^0 & \text{for } t^0 \geqslant \tau^0. \end{array} \right\} \tag{6.4}$$

Since φ^0 is a function of θ^0 and (a) it will also be a function of t^0 in the interval (6.1). The condition for the correctness of this description is that τ^0 is extremely large compared with the period of the system, i.e.

$$\tau^0 \gg l^0/\langle u^0\rangle^0, \tag{6.5}$$

where l^0 is the linear extension of the container and $\langle u^0\rangle^0$ is the mean value of the particle velocity.

We shall now calculate the mean force and the mean rate of work on the particle in the general system S, and let us start by considering the case where the a's are kept constant during the process. As we shall see, this simple case exhibits already the typical new features introduced by the theory of relativity. In non-relativistic thermodynamics the mechanical work is zero in such a process and the change of the temperature is due solely

to the supply of heat energy. In a relativistic theory, this is still true in the rest system S^0 but, as was shown in detail in reference 4, in any other system S we have a finite impulse and a finite work performed by the external forces. We shall now calculate this effect from statistical mechanics.

For simplicity we shall start by assuming that the relative velocity $\boldsymbol{v}$ is given by (5.2) so that (5.3) is the transformation connecting the phase-spaces $\Sigma(S)$ and $\Sigma(S^0)$. Then, using (5.19) and Jacobi's theorem (5.4,5), we get for the mean value of $\mathfrak{F}_x$ at the time t in S

$$\left.\begin{aligned}\langle\mathfrak{F}_x\rangle_t = \iint \frac{\mathfrak{F}_x^0 + \dfrac{v}{c^2}(\boldsymbol{\mathfrak{F}}^0 \cdot \boldsymbol{u}^0)}{1 + vp_x^0/E^0}\, \mathfrak{P}^0(\boldsymbol{p}^0, \boldsymbol{x}^0, \theta^0(t^0))(1 + vp_x^0/E^0)\boldsymbol{dp}^0\boldsymbol{dx}^0,\end{aligned}\right\} \quad (6.6)$$

where $\mathfrak{P}^0$ is the distribution function (6.2) (with constant α's). Here it must be remembered that $\theta^0(t^0)$ is a function of the variable

$$t^0 = t/\gamma - vx^0/c^2 \tag{6.7}$$

given by (5.7), which depends on the variable of integration x^0. Hence

$$\left.\begin{aligned}\langle\mathfrak{F}_x\rangle_t = &\iint\left(-\frac{\partial U^0(\boldsymbol{x}^0)}{\partial \boldsymbol{x}^0}\right)\mathfrak{P}^0(\boldsymbol{p}^0, \boldsymbol{x}^0, \theta^0(t^0))\boldsymbol{dp}^0\boldsymbol{dx}^0 \\ &+ v\iint\frac{(\boldsymbol{\mathfrak{F}}^0 \cdot \boldsymbol{p}^0)}{E^0}\,\mathfrak{P}(\boldsymbol{p}^0, \boldsymbol{x}^0, \theta^0(t^0))\boldsymbol{dp}^0\boldsymbol{dx}^0.\end{aligned}\right\} \quad (6.8)$$

The last integral is obviously zero since $\mathfrak{P}^0$ as a function of $(p_x^0, p_y^0, p_\gamma^0)$ depends on the squares of these quantities only. Therefore, it follows from (5.20) that the mean values of $\mathfrak{F}_x$ and $\mathfrak{K}_x$ are equal. In order to calculate the first integral in (6.8) we remark that the quantity $k\mathfrak{P}^0/\theta^0$, in the present case where the α's are constant, depends on the variable x^0 both through $U^0(\boldsymbol{x}^0)$, occurring in the exponential of the expression (6.2) for $\mathfrak{P}^0$, and through $\theta^0(t^0)$. Therefore

$$k\frac{\partial\,\mathfrak{P}^0/\theta^0}{\partial x^0} = \mathfrak{P}^0\left(-\frac{\partial U^0(\boldsymbol{x}^0)}{\partial x^0}\right) + k\frac{\partial(\mathfrak{P}^0/\theta^0)}{\partial\theta^0}\frac{\partial\theta^0(t^0)}{\partial x^0} \tag{6.9}$$

or, by means of the relation

$$\frac{\partial\theta^0(t^0)}{\partial x^0} = -\frac{\gamma v}{c^2}\frac{\partial\theta^0(t^0)}{\partial t} \tag{6.10}$$

following from (6.7),

$$k\frac{\partial \mathfrak{P}^0/\theta^0}{\partial x^0} = \left(-\frac{\partial U^0}{\partial x^0}\right)\mathfrak{P}^0 - k\frac{\gamma v}{c^2}\frac{\partial \mathfrak{P}^0/\theta^0}{\partial t}. \tag{6.11}$$

If we integrate this equation over the whole phase-space $\Sigma(S^0)$ the left hand side gives zero, while the integral of the first term on the right hand side is just the first term in (6.8). Hence

$$\langle \mathfrak{F}_x \rangle_t = \langle \mathfrak{K}_x \rangle_t = \frac{k\gamma v}{c^2}\frac{d}{dt}\int\int \frac{\mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,\theta^0(t^0))}{\theta^0(t^0)}\,\boldsymbol{dp}^0\boldsymbol{dx}^0. \tag{6.12}$$

Similarly we find, by means of (5.19,20),

$$\langle \mathfrak{F}_y \rangle_t = \langle \mathfrak{K}_y \rangle_t = 0, \quad \langle \mathfrak{F}_z \rangle_t = \langle \mathfrak{K}_z \rangle_t = 0 \tag{6.13}$$

which together with (6.12) may be written in the general vector form

$$\langle \boldsymbol{\mathfrak{F}} \rangle_t = \langle \boldsymbol{\mathfrak{K}} \rangle_t = \frac{k\gamma \boldsymbol{v}}{c^2}\frac{d}{dt}\int\int \frac{\mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,\theta^0(t^0))}{\theta^0(t^0)}\,\boldsymbol{dp}^0\boldsymbol{dx}^0. \tag{6.14}$$

In the same way we obtain for the mean mechanical effect

$$\langle \boldsymbol{\mathfrak{F}}\cdot\boldsymbol{u} \rangle_t = \langle \boldsymbol{\mathfrak{K}}\cdot\boldsymbol{v} \rangle_t = \frac{k\gamma v^2}{c^2}\frac{d}{dt}\int\int \frac{\mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,\theta^0(t^0))}{\theta^0(t^0)}\,\boldsymbol{dp}^0\boldsymbol{dx}^0. \tag{6.15}$$

For a gas of n particles, the expressions on the right hand sides of (6.14,15) have to be multiplied by n. For the impulse of the total mechanical force on the gas during a time interval $t_1 < t < t_2$ we get therefore

$$\left.\begin{aligned} \Delta\boldsymbol{I}(t_1,t_2) &= n\int_{t_1}^{t_2}\langle \boldsymbol{\mathfrak{F}} \rangle_t dt \\ &= \frac{n\gamma \boldsymbol{v} k}{c}\Big[\int\int \mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,\theta^0(t_2^0))/\theta^0(t_2^0)\boldsymbol{dp}^0\boldsymbol{dx}^0 \\ &\quad - \int\int \mathfrak{P}^0(\boldsymbol{p}^0,\boldsymbol{x}^0,\theta^0(t_1^0))/\theta^0(t_1^0)\boldsymbol{dp}^0\boldsymbol{dx}^0\Big]. \end{aligned}\right\} \tag{6.16}$$

where t_1^0 and t_2^0 are obtained from (6.7) by putting t equal to t_1 and t_2, respectively. Now choose t_1 and t_2 so that $t_1^0 \leq 0$ and $t_2^0 \geq \tau^0$ for all values of x^0 inside the container. Then, $\theta^0(t_2^0)$ and $\theta^0(t_1^0)$ have the constant values $\theta^0 + \Delta\theta^0$ and θ^0, respectively, in the two integrals in (6.16). Thus, we get for the mechanical impulse during the whole process

$$\left.\Delta \boldsymbol{I} = \frac{n\gamma \boldsymbol{v}}{c^2}\left[\frac{k}{\theta^0 + \Delta\theta^0} - \frac{k}{\theta^0}\right] = \gamma \boldsymbol{v}\frac{nk\Delta T^0}{c^2}.\right\} \tag{6.17}$$

Similarly, by integration of (6.15), we obtain the total external work

$$\Delta A = \frac{\gamma v^2}{c^2} nk\Delta T^0. \tag{6.18}$$

Hence

$$\Delta I_i = \left\{\frac{nk\Delta T^0}{c^2}\gamma \boldsymbol{v},\ -\frac{nk\Delta T^0}{c^2}\frac{\gamma v^2}{c}\right\} = \Delta g_i, \tag{6.19}$$

where Δg_i is the change of the quantity g_i in (5.17) for the case of constant $\boldsymbol{v}$.

From (5.17) and (6.19) we see that the difference $\Delta G_i - \Delta I_i$ is a 4-vector which, according to (1.1), must be interpreted as the four-momentum of supplied heat:

$$\Delta Q_i = \Delta G_i - \Delta I_i = \frac{\Delta H^0}{c^2} V_i = \frac{\Delta\langle \mathfrak{H}_g^0\rangle^0}{c^2} V_i = \frac{\Delta Q^0}{c^2} V_i \tag{6.20}$$

where

$$\Delta Q^0 = \Delta H^0 = \Delta\langle \mathfrak{H}_g^0\rangle^0 \tag{6.20'}$$

is the supplied heat in the rest system for constant (a).

The equation (6.20) is in agreement with the thermodynamical equation (1.4) derived in reference 4, but so far it has been derived from statistical mechanics only for the case where the a's are kept constant during the process. However, it is easy to find statistical expressions for the work and the impulse arising from an infinitesimal reversible change of the external parameters (a). In the system S^0, the work performed on a particle (for fixed $\boldsymbol{p}^0, \boldsymbol{x}^0$) by an increase (da_l) is given by (2.6,6'). The mean value of this quantity multiplied by n is to be identified with the work performed on the gas due to a change of the a's, i.e.

$$dA^0 = n\langle d_{(a)}\mathfrak{H}^0\rangle^0 = n\sum_l \langle\frac{\partial \mathfrak{H}^0}{\partial a_l}\rangle^0 da_l \tag{6.21}$$

or

$$dA^0 = \langle d_{(a)}\mathfrak{H}_g^0\rangle^0 = \sum_l \langle\frac{\partial \mathfrak{H}_g^0}{\partial a_l}\rangle^0 da_l \tag{6.22}$$

where $\mathfrak{H}_g^0$ is the total Hamiltonian (2.37) of the gas.

In the homogeneous case (5.25), there is only one external parameter

for which we can take the rest volume $\mathfrak{V}^0$. Since the work performed on a gas by a reversible increase $d\mathfrak{V}^0$ of the volume is

$$dA^0 = -\mathfrak{p}^0 d\mathfrak{V}^0, \tag{6.23}$$

a comparison with (6.21,22) gives

$$\mathfrak{p}^0 = -\langle \frac{\partial \mathfrak{H}_g^0}{\partial \mathfrak{V}^0} \rangle^0 = -n \langle \frac{\partial \mathfrak{H}^0(\boldsymbol{p}^0, \boldsymbol{x}^0, \mathfrak{V}^0)}{\partial \mathfrak{V}^0} \rangle^0, \tag{6.24}$$

an expression which also follows from (5.24) when one takes into account that the potential $U^0(\boldsymbol{x}^0)$ in the vicinity of the walls is a function of the normal distance to the wall.

On the analogy of (6.21,22), the impulse and work in S due to an increase (da_l) of the external parameters is equal to the mean value of the quantity $d_{(a)}P_i^g$ given by (2.39). Hence

$$\left.\begin{aligned} d_{(a)}I_i &= \langle d_{(a)}P_i^g \rangle = \sum_l da_l \langle \frac{\partial P_i^g(\xi, t, a)}{\partial a_l} \rangle = n \langle d_{(a)}P_i \rangle \\ &= n \sum_l da_l \langle \frac{\partial P_i(\boldsymbol{p}, \boldsymbol{x}, t, a)}{\partial a_l} \rangle = n \sum_l da_l \langle \frac{\partial U(x, a_l)}{\partial a_l} \rangle \frac{V_i}{c^2}. \end{aligned}\right\} \tag{6.25}$$

Since $\dfrac{\partial U}{\partial a_l}$ is a relativistic scalar, Jacobi's theorem (5.4,5) gives

$$\langle \frac{\partial U}{\partial a_l} \rangle = \langle \frac{\partial U^0}{\partial a_l} \rangle^0 = \langle \frac{\partial \mathfrak{H}^0}{\partial a_l} \rangle^0.$$

Thus, by (6.21,22,25),

$$d_{(a)}I_i = \frac{dA^0}{c^2} V_i = \frac{\langle d_{(a)}\mathfrak{H}_g^0 \rangle^0}{c^2} V_i, \tag{6.26}$$

which shows that this part of the mechanical 'impulse-work' dI_i is a 4-vector. For an *infinitesimal* reversible process the total expression for dI_i is obtained by combining (6.26) with the equation (6.19), i.e.

$$\left.\begin{aligned} dI_i &= dg_i + \frac{dA^0}{c^2} V_i \\ dg_i &= \left\{ \frac{nkdT^0}{c^2} \gamma \boldsymbol{v}, \; -\frac{nkdT^0}{c^2} \frac{\gamma v^2}{c} \right\} \end{aligned}\right\} \tag{6.27}$$

for constant $\boldsymbol{v}$. Instead of (6.20) we now get in the general case

$$dQ_i = dG_i - dI_i = \frac{dH^0 - dA^0}{c^2} V_i = \frac{dQ^0}{c^2} V_i, \tag{6.28}$$

in complete agreement with (1.4). The statistical expression for the transferred heat energy in S^0 is, by (5.15) and (6.22),

$$dQ^0 = dH^0 - dA^0 = d\langle \mathfrak{H}_g^0 \rangle^0 - \sum_l da_l \langle \frac{\partial \mathfrak{H}_g^0}{\partial a_l} \rangle^0. \tag{6.29}$$

Since $dg_i \cdot V^i = 0$ we get from (6.27)

$$V^i dg_i = -dA^0 \tag{6.30}$$

which, by means of (1.2,3), gives

$$dA = \boldsymbol{v} d\boldsymbol{I} + dA^0 \sqrt{1 - v^2/c^2}. \tag{6.31}$$

The error made in the early treatments of relativistic thermodynamics consisted in replacing $d\boldsymbol{I}$ in this expression by $d\boldsymbol{G}$ instead of the correct replacement of $d\boldsymbol{I} = d\boldsymbol{G} - d\boldsymbol{Q}$ following from (1.1).

In the homogeneous case (5.25), where (5.28) and (6.23) are valid, we get from (6.27), (1.2,3) and (6.31)

$$\left.\begin{aligned} d\boldsymbol{I} &= \frac{\mathfrak{V}^0 d\mathfrak{p}^0}{c^2} \gamma \boldsymbol{v} \\ dA &= \frac{\mathfrak{V}^0 d\mathfrak{p}^0}{c^2} \gamma v^2 - \mathfrak{p} d\mathfrak{V}, \end{aligned}\right\} \tag{6.32}$$

where

$$\mathfrak{V} = \mathfrak{V}^0 \sqrt{1 - v^2/c^2}, \quad \mathfrak{p} = \mathfrak{p}^0 \tag{6.33}$$

is the volume and pressure in the system S. (6.32) is in agreement with the equations (66) and (72) in reference 4.

The equation (4.6), which for a canonical ensemble (4.17) reads

$$\iint e^{[\varphi + \theta^i P_i(p, x, t, a)]/k} \boldsymbol{dpdx} = 1, \tag{6.34}$$

determines φ as a function of the state variables θ^i and (a). Differentiation of this equation gives for infinitesimal increases $d\theta^i$, (da_l) of these variables

$$\iint (d\varphi + d\theta^i P_i + \theta^i d_{(a)} P_i) \mathfrak{P} \boldsymbol{dpdx} = 0$$

or

$$d\varphi + d\theta^i \langle P_i \rangle + \theta^i \langle d_{(a)} P_i \rangle = 0. \tag{6.35}$$

Further, by differentiation of the equation

$$k\langle\eta\rangle = \varphi + \theta^i\langle P_i\rangle \tag{6.36}$$

we get, using (6.35),

$$\left.\begin{aligned} kd\langle\eta\rangle &= d\varphi + d\theta^i\langle P_i\rangle + \theta^i d\langle P_i\rangle \\ &= \theta^i(d\langle P_i\rangle - \langle d_{(a)}P_i\rangle). \end{aligned}\right\} \tag{6.37}$$

Multiplying this equation with $-n$ we obtain, by (5.36), (5.15) and (6.25), for the change of the entropy S

$$dS = -\theta^i(dG_i - d_{(a)}I_i). \tag{6.38}$$

For the type of process considered here, where $\boldsymbol{v}$ is constant, we have $\theta^i dg_i = \frac{1}{T^0} V^i dg_i = 0$.

Thus, by means of (6.26–28),

$$dS = -\theta^i(dG_i - dI_i) = -\theta^i dQ_i \tag{6.39}$$

in accordance with the thermodynamical equation (1.17) for a reversible process. This may be regarded as a new proof of the statistical expression (5.36) for the entropy.

Finally, a few words about the process of *adiabatic acceleration* of the thermodynamic body, where the acceleration is performed 'infinitely' slowly and smoothly with constant (a) and without heat supply. In that case we may assume that the internal thermodynamic state is the same in the successive momentary rest systems S^0 of the container which means that H^0 and $\theta^0 = 1/T^0$ are constant during the process.

From (5.17), which also may be written

$$G_i = \frac{H^0 + nkT^0}{c^2} V_i + \frac{nkT^0}{c\gamma} \delta_{i4}, \tag{6.40}$$

we then get

$$\Delta G_i = \frac{H^0 + nkT^0}{c^2} \Delta V_i + \frac{nkT^0}{c} \delta_{i4} \Delta\gamma^{-1} = \Delta I_i \tag{6.41}$$

since there is no heat supply in this process. For an infinitesimal process of this type we have, since $V^i dV_i = 0$,

$$V^i dI_i = \frac{nkT^0}{c} V^4 d\gamma^{-1} = nkT^0\gamma\, d\gamma^{-1}$$

or by (1.2,3)

$$dA = \boldsymbol{v}d\boldsymbol{I} - nkT^0 d\gamma^{-1} \tag{6.42}$$

which replaces (6.31) in this case. A detailed statistical derivation of (6.41) is most adequately obtained by replacing the successive rest systems by one smoothly accelerated system of coordinates such as the one introduced in chapter VIII, § 97, of reference 9. This requires a generalization of the statistical mechanics of the preceding sections to the case of accelerated systems of reference, a subject which we shall not go into here. However, in the next section we shall at least give a statistical derivation of the equation (1.17) for a process of adiabatic acceleration in which case (1.17) reduces to $dS = 0$.

7. Mean Values in a Canonical Ensemble

According to (4.10,17) a gas of n particles in thermal equilibrium is, in an arbitrary system of inertia S, described by the canonical probability density

$$\mathfrak{P} = e^{[\Phi + \theta^i P_i^g]/k}, \tag{7.1}$$

where

$$\left.\begin{aligned} P_i^g &= p_i^g + \frac{V_i}{c^2} U_g \\ p_i^g &= \sum_{r=1}^{n} p_i^{(r)}, \qquad U_g = \sum_{r=1}^{n} U(\boldsymbol{x}^{(r)}, t, a). \end{aligned}\right\} \tag{7.2}$$

Thus, the 'total canonical momentum' P_i^g of the gas depends on the 'coordinates' (ξ_μ) (3.26) of the points in phase-space and on the parameters V^i and (a_l) of the thermodynamical state, i.e.

$$P_i^g = P_i^g(\xi_\mu, t, V^i, a). \tag{7.3}$$

The quantity Φ, which is connected with the free energy by (4.14, 18), is defined by the equation

$$\left.\begin{aligned} \int \cdot\cdot \int e^{[\Phi + \theta^i P_i^g(\xi, t, V^i, a)]/k} d\xi &= 1, \\ d\xi &= \boldsymbol{dp}^{(1)}\boldsymbol{dx}^{(1)} \ldots\ldots \boldsymbol{dp}^{(n)}\boldsymbol{dx}^{(n)} \end{aligned}\right\} \tag{7.4}$$

or

$$e^{-\Phi/k} = \int \cdot\cdot \int \exp[\theta^i P_i^g(\xi, t, V^i, a)] d\xi. \tag{7.5}$$

The variables θ^i and V^i are connected by (4.16). However, for the following development it is more convenient at the moment to regard the variables θ^i and V^i as independent of each other. For fixed V^i the quantity Φ, as defined by (7.5), appears then as a function $\Phi(\theta^i, V^i, a)$ of the independent variables θ^i and (a_l), which may be partially differentiated with respect to θ^i or to a_l all other quantities being kept constant in these derivations.

By partial differentiation of (7.4) with respect to θ^i we then get

$$\int \cdot \cdot \int \left(\frac{\partial \Phi(\theta^i, V^i, a)}{\partial \theta^i} + P_i^g \right) \mathfrak{P} d\xi = 0. \tag{7.6}$$

Thus, taking account of (7.1,4) and the relations (5.15) and (4.16),

$$G_i = \langle P_i^g \rangle = - \left[\frac{\partial \Phi(\theta^i, V^i, a)}{\partial \theta^i} \right]. \tag{7.7}$$

Here and in the following, a square bracket around a function of (θ^i, V^i, a) indicates that we have to put

$$\theta^i = \theta V^i = \theta^0 V^i \tag{7.8}$$

in this function.

Further partial differentiation of (7.6) with respect to θ^k gives

$$\int \cdot \cdot \int \left\{ \frac{\partial^2 \Phi}{\partial \theta^i \partial \theta^k} + \frac{1}{k} \left(\frac{\partial \Phi}{\partial \theta^i} + P_i^g \right) \left(\frac{\partial \Phi}{\partial \theta^k} + P_i^g \right) \right\} \mathfrak{P} d\xi = 0 \tag{7.9}$$

or, if we put $\theta^i = \theta V^i$ in this equation and use (7.7),

$$\langle (P_i^g - \langle P_i^g \rangle)(P_k^g - \langle P_k^g \rangle) \rangle = - k \left[\frac{\partial^2 \Phi(\theta^i, V^i, a)}{\partial \theta^i \partial \theta^k} \right]. \tag{7.10}$$

In particular for $k = i$ we get the following simple expression for the square of the fluctuation $\sigma\{P_i^g\}$ of the quantity P_i^g:

$$\sigma^2\{P_i^g\} = - k \left[\frac{\partial^2 \Phi(\theta^i, V^i, a)}{\partial \theta^{i2}} \right]. \tag{7.11}$$

Similarly, the mean value of the probability exponential or the entropy may be expressed in terms of Φ and its first order derivatives. From (5.36,37) and (7.7), we get

$$\left.\begin{aligned} S &= -k\langle\eta_g\rangle = -[\Phi + \theta^i\langle P_i^g\rangle] \\ &= -\left[\Phi(\theta^i, V^i, a) - \theta^i \frac{\partial\Phi(\theta^i, V^i, a)}{\partial\theta^i}\right]. \end{aligned}\right\} \quad (7.12)$$

Partial differentiation of (7.4) with respect to a_l (constant θ^i, V^i) gives

$$\int\cdot\cdot\int\left(\frac{\partial\Phi}{\partial a_l} + \frac{\theta^i V_i}{c^2}\frac{\partial U_g}{\partial a_l}\right)\mathfrak{P}d\xi = 0. \quad (7.13)$$

Thus, putting $\theta^i = \theta V^i$ we get, since $\frac{\partial U_g}{\partial a_l}$ is invariant,

$$\left.\begin{aligned} \left\langle\frac{\partial U_g}{\partial a_l}\right\rangle &= \left\langle\frac{\partial U_g^0}{\partial a_l}\right\rangle^0 = \left\langle\frac{\partial \mathfrak{H}_g^0}{\partial a_l}\right\rangle^0 \\ &= \theta^{-1}\left[\frac{\partial\Phi(\theta^i, V^i, a)}{\partial a_l}\right] = \theta^{0-1}\frac{\partial\Phi^0(\theta^0, a)}{\partial a_l} \end{aligned}\right\} \quad (7.14)$$

where $\Phi^0(\theta^0, a) = n\varphi^0(\theta^0, a)$ is the function defined by (4.13). In the homogeneous case, where the rest volume $\mathfrak{V}^0$ can be identified with the external parameter a, (5.29), (6.24) and (7.14) gives the following expression for the pressure

$$\mathfrak{p} = \mathfrak{p}^0 = -\theta^{-1}\left[\frac{\partial\Phi(\theta^i, V^i, \mathfrak{V}^0)}{\partial\mathfrak{V}^0}\right] = -\theta^{0-1}\frac{\partial\Phi^0(\theta^0, \mathfrak{V}^0)}{\partial\mathfrak{V}^0}. \quad (7.15)$$

From the preceding considerations it follows that all the thermodynamic functions of the system can be calculated by simple differentiations when the function $\Phi(\theta^i, V^i, a)$ is known. Also typically statistical quantities like the fluctuations of P_i^g may be obtained in this way. For reversible processes we may then also express quantities such as dI_i and dQ_i in terms of Φ and its derivations. For instance we get from (6.22,26) and (7.14)

$$\left.\begin{aligned} dA^0 &= \theta^{0-1}\sum_e \frac{\partial\Phi^0(\theta^0, a)}{\partial a_l} da_l \\ d_{(a)}I_i &= \left(\theta^{0-1}\sum_e \frac{\partial\Phi^0(\theta^0, a)}{\partial a_l} da_l\right) V_i/c^2. \end{aligned}\right\} \quad (7.16)$$

We shall now investigate the general structure of the function $\Phi(\theta^i, V^i, a)$. Although this function for $\theta^i = \theta V^i$ of course has the same value in every

Lorentz system, it is *not* a form-invariant function of the (independent) 4-vectors θ^i and V^i. Since

$$\theta^i P_i^g = \theta^i p_i^g + \frac{\theta^i V_i}{c^2} U_g \tag{7.17}$$

is a sum of two parts containing the momenta and coordinates separately, we may write

$$e^{-\Phi/k} = e^{-\Phi_p/k} e^{-\Phi_q/k}, \qquad \Phi = \Phi_p + \Phi_q, \tag{7.18}$$

where

$$e^{-\Phi_p(\theta^i)/k} = \int \ldots \int e^{\theta^i p_i^g/k} \boldsymbol{dp}^{(1)} \ldots \boldsymbol{dp}^{(n)} \tag{7.19}$$

is a function of θ^i only, while

$$e^{-\Phi_q(\theta^i, V^i, a)} = \int \ldots \int e^{\theta^i V_i U_g/kc^2} \boldsymbol{dx}^{(1)} \ldots \boldsymbol{dx}^{(n)} \tag{7.20}$$

in general depends on all variables (θ^i, V^i, a).

By partial differentiation of (7.19) with respect to θ^i we get, similarly as in (7.6,7), for the mean value of the linear four-momentum p_i^g

$$\langle p_i^g \rangle = -\left[\frac{\partial \Phi_p(\theta^i)}{\partial \theta^i}\right] \tag{7.21}$$

which may be interpreted as the 'bare' four-momentum of the gas. Similarly as in (7.11), the square of the fluctuation of the linear four-momentum is

$$\sigma^2\{p_i^g\} = -k\left[\frac{\partial^2 \Phi_p(\theta^i)}{\partial \theta^{i2}}\right]. \tag{7.22}$$

By subtraction of (7.7) and (7.21) and by using (7.2) and (7.18) we get for the 'four-momentum of the potential energy'

$$\frac{\langle U_g \rangle}{c^2} V^i = \frac{\langle U_g^0 \rangle^0}{c^2} V_i = -\left[\frac{\partial \Phi_q(\theta^i, V^i, a)}{\partial \theta^i}\right]. \tag{7.23}$$

Since $p_i^g = \sum_r p_i^{(r)}$ is the sum of the four-momenta of the separate particles we obtain from (7.19)

$$\Phi_p(\theta^i) = n\varphi_p(\theta^i) \tag{7.24}$$

where $\varphi_p(\theta^i)$ is given by

$$e^{-\varphi_p(\theta^i)/k} = \int e^{\theta^i p_i/k} d\boldsymbol{p}. \tag{7.25}$$

Here, both p_i and

$$\theta^i = \{\boldsymbol{\theta}, \theta^4\} \tag{7.26}$$

are time-like 4-vectors.

In the intergral (7.25) it is convenient as new variables of integration to introduce the components of the momentum vector $\boldsymbol{p}^0$ in a Lorentz system S^0 which has its time axis in the direction of θ^i. Then, the four-velotity of S^0 relative to S is

$$V^i = \theta^i/\theta = \{\boldsymbol{V}, V^4\} \tag{7.27}$$

which in S^0 has the components

$$V^{0i} = c\delta^{i4}. \tag{7.28}$$

Hence

$$\left.\begin{aligned} \theta^i p_i &= \theta V^i p_i = \theta V^{0i} p_i^0 = \theta c p_4^0 \\ &= -\theta E^0 = -\theta c \sqrt{m^2c^2 + |\boldsymbol{p}^0|^2}. \end{aligned}\right\} \tag{7.29}$$

Since $d\boldsymbol{p}/E$ is known to be invariant under Lorentz transformations, the Jacobian corresponding to the transformation $\boldsymbol{p} \to \boldsymbol{p}^0$ is (comp. equation (2.35))

$$\frac{d(\boldsymbol{p})}{d(\boldsymbol{p}^0)} = \frac{E}{E^0} = V^4/c + (\boldsymbol{V}\cdot\boldsymbol{p}^0)/E^0 = \theta^4/c\theta + (\boldsymbol{\theta}\cdot\boldsymbol{p}^0)/\theta E^0 \tag{7.30}$$

on account of (7.27). Thus, (7.25) becomes

$$e^{-\varphi_p(\theta^i)/k} = \int e^{-\theta E^0/k} \frac{\theta^4}{\theta c} d\boldsymbol{p}^0 + \int e^{-\theta E^0/k} \frac{\boldsymbol{\theta}\cdot\boldsymbol{p}^0}{\theta E^0} d\boldsymbol{p}^0.$$

The last integral is obviously zero, so that $e^{-\varphi_p/k}$ is of the form

$$e^{-\varphi_p(\theta^i)/k} = \frac{\theta^4}{c\theta} e^{-f_p(\theta)/k}. \tag{7.31}$$

Here $f_p(\theta)$ is a function of the invariant norm

$$\theta = \sqrt{-\theta_i\theta^i}/c \tag{7.32}$$

defined by

$$e^{-f_p(\theta)/k} = \int e^{-\theta E^0/k} d\boldsymbol{p}^0 = (mc)^3 \iiint e^{-\frac{\theta mc^2}{k}\sqrt{1+\xi^2+\eta^2+\zeta^2}} d\xi d\eta d\zeta. \tag{7.33}$$

A comparison of (7.33) with (4.13) shows that

$$\varphi_p^0(\theta^0) = f_p(\theta^0). \tag{7.34}$$

The function $f_p(\theta)$ defined by (7.33) may be expressed in terms of a Hankel function $H_2^{(1)}$ of the first kind and the second order with imaginary argument [11] in the following way:

$$\left.\begin{aligned} e^{-f_p(\theta)/k} &= (mc)^3 4\pi \int_0^\infty e^{-\frac{\theta mc^2}{k}\sqrt{1+u^2}} u^2 du \\ &= \frac{2\pi^2 m^2 ck}{i\theta} H_2^{(1)}(imc^2\theta/k). \end{aligned}\right\} \tag{7.35}$$

From (7.24,31) we get for the part Φ_p of Φ

$$\Phi_p(\theta^i) = n\varphi_p(\theta^i) = n\left(f_p(\theta) - k\ln\frac{\theta^4}{\theta c}\right). \tag{7.36}$$

This part is independent of the forces acting on the system, which have an influence only on the part Φ_q defined by (7.20).

For a system of non-interacting particles, where the potential is of the form (7.2), we have on the analogy of (7.24)

$$\Phi_q(\theta^i, V^i, a) = n\varphi_q(\theta^i, V^i, a) \tag{7.37}$$

with

$$e^{-\varphi_q/k} = \int e^{\theta^i V_i U(\boldsymbol{x},t,a)/kc^2} \boldsymbol{dx}. \tag{7.38}$$

If we introduce the coordinates $\boldsymbol{x}^0$ of the rest system S^0 instead of $\boldsymbol{x}$ as integration variables, we have in the integral (7.38), which is performed at constant t, to put

$$\boldsymbol{dx} = \boldsymbol{dx}^0\sqrt{1 - v^2/c^2} = \frac{c}{V^4}\boldsymbol{dx}^0. \tag{7.39}$$

Thus, (7.38) may be written

$$e^{-\varphi_q(\theta^i, V^i, a)/k} = e^{-f_q(\mu,a)/k} c/V^4, \tag{7.40}$$

where $f_q(\mu,a)$, defined by

$$e^{f_q(\mu,a)/k} = \int e^{-\mu U^0(\boldsymbol{x}^0, a)/k} \boldsymbol{dx}^0, \tag{741}$$

is an invariant function of (a) and of the invariant variable

$$\mu = -\theta^i V_i/c^2. \tag{7.42}$$

A comparison of (7.41) with (4.13) shows that

$$\varphi_q^0(\theta^0, a) = f_q(\theta^0, a). \tag{7.43}$$

The quantity μ is positive for θ^i in the vicinity of the value (7.8). From (7.40,36,18) we finally get

$$\left.\begin{aligned} \Phi_q &= n\left(f_q(\mu, a) - k\ln\frac{c}{V^4}\right) \\ \Phi(\theta^i, V^i, a) &= n\left(f_p(\theta) + f_q(\mu, a) - k\ln\frac{\theta^4}{\theta V^4}\right) \end{aligned}\right\} \tag{7.44}$$

By means of this expression for Φ, we may now calculate the mean values of various physical quantities. For instance, by (7.7), the four-momentum G_i is obtained by differentiation of Φ with respect to θ^i and subsequently putting $\theta^i = \theta V^i$. Since

$$\frac{\partial\theta}{\partial\theta^i} = -\frac{\theta_i}{c^2\theta}, \quad \frac{\partial\mu}{\partial\theta^i} = -V_i/c^2, \tag{7.45}$$

we get

$$\left.\begin{aligned} \frac{\partial\Phi}{\partial\theta^i} &= n(-f_p'(\theta)\theta^i/\theta - f_q'(\mu, a)V_i)/c^2 - nk\left(\frac{\delta_{i4}}{\theta^4} + \frac{\theta_i}{c^2\theta^2}\right), \\ f_q'(\mu, a) &= \frac{\partial f_q(\mu, a)}{\partial\mu}. \end{aligned}\right\} \tag{7.46}$$

Thus, since

$$[\mu] = \theta = \theta^0, \tag{7.47}$$

$$G_i = -\left[\frac{\partial\Phi}{\partial\theta^i}\right] = n(f_p'(\theta^0) + f_q'(\theta^0, a))V_i/c^2 + \frac{nk}{\theta^0}\frac{V_i}{c^2} + \frac{nk}{\theta^0\gamma c}\delta_{i4} \tag{7.48}$$

which expresses G_i as function of the thermodynamical variables (V_i, a) and $\theta^0 = 1/T^0$. In the rest system where $V_i^0 = -c\delta_{i4}$, we get of course $\boldsymbol{G}^0 = 0$, and

$$H^0 = -cG_4^0 = n(f_p'(\theta^0) + f_q'(\theta^0, \mathrm{a})) \tag{7.49}$$

so that (7.48) may be written

$$G_i = \frac{H^0 + nkT^0}{c^2}V_i + \frac{nkT^0}{c\gamma}\delta_{i4}, \tag{7.50}$$

in accordance with (6.40).

By further differentiation of (7.46) with respect to θ^i, we get from (7.11) an expression for the square of the fluctuation of P_i^g which obviously increases linearly with n. Since also the mean values, i.e. G_i, are linearly dependent on n we have for the ratio

$$\frac{\sigma\{P_i^g\}}{\langle P_i^g\rangle} = O(n^{-1/2}) \tag{7.51}$$

so that the fluctuations, generally speaking, become unimportant for macroscopic bodies. As mentioned earlier this is a general feature for all thermodynamic quantities.

When we put $V^i = \theta^i/\theta$ in $\Phi(\theta^i, V^i, a)$, we get a function $\Phi(\theta^i, a)$ of θ^i and (a) which, according to (7.44,42), is given by

$$\Phi(\theta^i, a) = [\Phi(\theta^i, V^i, a)] = n(f_p(\theta) + f_q(\theta, a)). \tag{7.52}$$

Thus, as a function of the thermodynamical state variables (θ^i, a) the quantity Φ is a function of the norm θ and (a) only:

$$\left.\begin{aligned} \Phi(\theta^i, a) &= f(\theta, a), \\ f(\theta, a) &= n(f_p(\theta) + f_q(\theta, a)). \end{aligned}\right\} \tag{7.53}$$

For the corresponding quantity Φ^0 in the rest system, defined by (4.10–13), we get by (7.34, 43)

$$\Phi^0(\theta^0, a) = n\varphi^0(\theta^0, a) = n(\varphi_p^0 + \varphi_q^0) = n(f_p(\theta^0) + f_q(\theta^0, a))$$

or

$$\Phi^0(\theta^0, a) = f(\theta^0, a). \tag{7.54}$$

Since $\theta = \theta^0$ is an invariant, (7.53, 54) show that

$$\Phi(\theta^i, a) = \Phi^0(\theta, a) = \Phi^0(\theta^0, a), \tag{7.55}$$

in accordance with (4.18).

As we have seen, the equation (7.7) allows us to calculate the four-momentum G_i by differentiating the function $\Phi(\theta^i, V^i, a)$ with respect to θ^i and afterwards using the relation (7.8). However, if we use (7.8) first in $\Phi(\theta^i, V^i, a)$, by which we obtain the function $\Phi(\theta^i, a)$ given by (7.53), and subsequently differentiate with respect to θ^i we get a quantity

$$P_i = -\frac{\partial\Phi(\theta^i, a)}{\partial\theta^i} \tag{7.56}$$

which, in contrast to G_i, is a 4-vector. In fact, from (7.53, 45, 8) we obtain

$$P_i = \frac{\partial f(\theta, a)}{\partial \theta} \frac{\theta_i}{c^2 \theta} = n(f_p'(\theta^0) + f_q'(\theta^0, a)) V_i / c^2$$

or, by means of (7.49),

$$P_i = \frac{H^0}{c^2} V_i . \tag{7.57}$$

P_i would be the four-momentum if the system were a free system.

In conclusion we shall convince ourselves that the expression (7.12) for the entropy is independent of V^i. From (7.46,8,53) we get

$$\left[\theta^i \frac{\partial \Phi}{\partial \theta^i}\right] = \theta n(f_p'(\theta) + f_q'(\theta, a) = \theta f'(\theta, a) \tag{7.58}$$

and, hence, for the entropy (7.12)

$$S = -f(\theta, a) + \theta \frac{\partial f(\theta, a)}{\partial \theta} . \tag{7.59}$$

We see that this expression is independent of V^i, i.e.

$$S = S^0$$

in accordance with the invariance property of the entropy. Further it follows that S is unchanged, i.e.

$$dS = 0 \tag{7.60}$$

under an adiabatic acceleration, where θ and (a) are constant and only the variables V^i are changed. (7.60) is in accordance with the thermodynamic relation (1.17) for the process in question.

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References

1. H. Ott, Zs. f. Phys. **175**, 70 (1963).
2. M. Planck, Berl. Ber. p. 542 (1907); Ann. d. Phys. **76**, 1 (1908);
   F. Hasenöhrl, Wien. Ber. **116**, 1391 (1907);
   A. Einstein, Jahrb. f. Rad. und El. 4, 411 (1907) and numerous textbooks on relativity theory.
3. H. Arzeliès, Nuovo Cimento **35**, 792 (1965);
   R. Penney, Nuovo Cimento **43** A, 911 (1966);
   T. W. B. Kibble, Nuovo Cimento **41** B, 72, 83, 84 (1966);
   A. Gamba, Nuovo Cimento **37**, 1792 (1965); **41** B, 72 (1966);
   H. Arzeliès, Nuovo Cimento **41** B, 81 (1966);
   F. Rohrlich, Nuovo Cimento **45** B, 76 (1966);
   L. de Broglie, Compt. Rend. **262**, 1235 (1966);
   A. Starnszkievicz, Act. Phys. Pol. **29**, 249 (1966);
   L. A. Schmid, Nuovo Cimento **47** B, 1 (1967);
   P. T. Landsberg, Proc. Phys. Soc. **89**, 1007 (1966).
4. C. Møller, Mat. Fys. Medd. Dan. Vid. Selsk. **36**, 1 (1967).
5. I. Brevik, Mat. Fys. Medd. Dan. Vid. Selsk. **36**, 3 (1967).
6. L. Söderholm, The Transformation Properties of Momentum and Energy of the Heat Supplied to an Elastic System in a Process According to Special Relativistic Thermodynamics (1968) (to be published in Nuovo Cimento).
7. See the first paper by Arzeliès quoted in ref. 3.
8. C. Møller, Thermodynamics in the Special and the General Theory of Relativity (1967) in 'Old and New Problems in Elementary Particles', Academic Press, New York and London, 1968.
9. See, for instance, C. Møller, The Theory of Relativity, Oxford (1952), § 21, Eq. (56).
10. F. Lurçat and P. Mazur, Nuovo Cimento **31**, 140 (1964);
    A. O. Barut, Phys. Rev. **109**, 1376 (1958).
11. F. Jüttner, Ann. d. Phys. **34**, 856 (1911), which contains a relativistic treatment of an ideal gas in the rest system.

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