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THE THERMODYNAMICAL  
POTENTIALS IN THE THEORY OF  
RELATIVITY AND THEIR  
STATISTICAL INTERPRETATION

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## Synopsis

In the theory of relativity the thermodynamical state of a homogeneous isotropic body is determined by five independent variables. In the present paper it is shown that the thermodynamical properties of the body are completely determined by relativistically invariant functions  $\Phi$  and  $\Psi$  of the state variables, which are the appropriate generalizations of the classical free energies of Helmholtz and Gibbs. When the 'potential'  $\Phi$  (or  $\Psi$ ) is given, all thermodynamical quantities, such as the four-momentum, entropy etc., can be obtained by partial differentiations of the potentials with respect to the state variables. Finally it is shown that the potentials  $\Phi$  and  $\Psi$  have a simple statistical interpretation in the relativistic generalization of Gibbs' classical statistical mechanics, which allows to calculate the functions  $\Phi$  and  $\Psi$  when the mechanical constitution of the system is known.

## 1. Introduction and Survey

In classical non-relativistic thermodynamics the thermodynamical potentials —the free energies of HELMHOLTZ and GIBBS— play an important role. When a potential is given as a function of the thermodynamical state variables all state functions can be obtained by partial differentiations of the potential, i.e. the thermodynamical properties of the body in question are completely determined by the potentials. For a homogeneous isotropic body *at rest* and in thermal equilibrium the state is determined by two variables, for instance the volume  $V^0$  and the temperature  $T^0$ , and the free energy of HELMHOLTZ is defined by

$$F^0 = H^0 - T^0 S^0, \quad (1.1)$$

where  $H^0$  and  $S^0$  are the energy and the entropy, respectively. When  $F^0$  is known as a function of  $T^0$  and  $V^0$ , the entropy and pressure are given by

$$S^0 = - \frac{\partial F^0(T^0, V^0)}{\partial T^0}, \quad p^0 = - \frac{\partial F^0(T^0, V^0)}{\partial V^0}, \quad (1.2)$$

and by (1.1) it follows for the energy

$$H^0 = F^0 - T^0 \frac{\partial F^0(T^0, V^0)}{\partial T^0}. \quad (1.3)$$

In a relativistic theory, the relations (1.2) must still be valid in the rest system  $S^0$  of the body, but there is no a priori reason that the same relations should hold in every system of inertia  $S$ . The principle of relativity requires only that the corresponding relativistic relations must be covariant and must reduce to (1.2) in the rest system. Nevertheless, PLANCK in his classical paper [1] tried to determine transformation laws for the thermodynamical quantities in such a way that relations of the form (1.2) remain valid in

every system of inertia  $S$ . If  $v$  is the velocity of the body (or of  $S^0$ ) with respect to  $S$ , we have

$$p = p^0, \quad V = V^0\sqrt{1 - \beta^2}, \quad \beta = v/c. \quad (1.4)$$

The pressure is relativistically invariant, and the same is assumed for the entropy, i.e.

$$S = S^0. \quad (1.5)$$

In order that relations (1.2) be valid also for the transformed quantities, we have then to accept PLANCK's transformation laws for the free energy and temperature in the form

$$F = F^0\sqrt{1 - \beta^2} \quad (1.6)$$

$$T_P = T^0\sqrt{1 - \beta^2}, \quad (1.7)$$

In fact, from (1.2 -7) one easily finds the relations

$$S = -\frac{\partial F(T_P, V)}{\partial T_P}, \quad p = -\frac{\partial F(T_P, V)}{\partial V} \quad (1.8)$$

which have the same form as the equations (1.2) valid in the rest system.

By this argument PLANCK was led to introduce a temperature  $T_P$  relative to the arbitrary system of inertia  $S$  given by the formula (1.7) and his point of view has been accepted again quite recently in a paper by R. BALESCU [2]. However, in the meantime H. OTT [3] had given strong arguments for introducing a different temperature  $T_O$  given by

$$T_O = T^0/\sqrt{1 - \beta^2}. \quad (1.9)$$

In fact, this formula follows uniquely (see (1.35)) if one wants the second law for reversible processes to have the same form

$$dS = \frac{dQ_{\text{rev}}}{T_O} \quad (1.10)$$

as in the rest system, where we have

$$dS^0 = \frac{dQ_{\text{rev}}^0}{T^0}. \quad (1.11)$$

The violent discussions in the literature following Ott's paper have made it clear that the relativity principle alone does not lead to a unique concept of temperature relative to an arbitrary system  $S$ , for the transformation law for the temperature will depend on which of the classical thermodynamical relations holding in the rest system, are assumed to retain their form under Lorentz transformations. Beforehand it does not seem quite natural to base the definition of temperature on the requirement of form-invariance of the relations (1.2, 8). Firstly, they refer to the rather special case of a homogeneous isotropic body and it would seem more natural to postulate the form-invariance of the first and the second laws of thermodynamics which are believed to be valid for any thermodynamic system. Secondly, in an arbitrary system of inertia the definition of the state of a homogeneous and isotropic body requires the fixation of five (not two) independent variables, for instance besides  $T^0$  and  $V^0$  the three components of the velocity  $\mathbf{v}$ . This is also the case in the non-relativistic theory, but there the internal thermodynamic properties are entirely separated from the external kinetic properties of the body. This is not so in relativity theory since the inertial mass of the body depends on the internal state. Therefore it is to be expected that the pertinent relativistic generalization of the equations (1.2) will consist of *five* equations which express five thermodynamical quantities as partial derivatives of the relativistic potentials with respect to five suitably chosen independent state variables. These equations must of course reduce to the two equations (1.2) in the rest system  $S^0$ .

In section 2 of the present paper we shall see that these expectations are fulfilled when we use the formulation of relativistic thermodynamics which, as was shown in a recent paper [4], is suggested by relativistic statistical mechanics. In the remaining part of the present section we shall give a short account of the relativistic formulation of the first and the second laws obtained in the just quoted paper.

In view of the above mentioned arbitrariness in the general definition of the temperature, it was proposed to abandon the notion of a separate temperature relative to the different systems of inertia. Therefore, when we speak of the temperature of the body we simply mean the proper temperature as measured by a thermometer at rest in the body. In any system of inertia  $S$  different from  $S^0$  it appears more adequate to speak of a temperature 4-vector  $T^i$  as defined by ARZELIÈS [5]. If  $V^i$  is the four-velocity of the body with components

$$V^i = \{\gamma\mathbf{v}, \gamma c\}, \quad \gamma = (1 - \beta^2)^{-\frac{1}{2}} \quad (1.12)$$

the temperature vector is

$$T^i = T^0 V^i / c. \quad (1.13)$$

In the rest system this 4-vector has only the one non-vanishing component  $T^{04}$  which is equal to the proper temperature  $T^0$ . In an arbitrary system  $S$  the fourth component  $T^4$  is equal to the Ott temperature (1.9).

In many thermodynamical considerations it is more convenient to introduce the reciprocal proper temperature

$$\theta = 1/T^0 \quad (1.14)$$

as a measure of the thermal state. Then, if we also introduce a function

$$\Phi^0(\theta^0, V^0) = \theta^0 F^0 \quad (1.15)$$

( $-\Phi^0$  is the so-called Planck potential), the relations (1.2) take the form

$$H^0 = \frac{\partial \Phi^0(\theta^0, V^0)}{\partial \theta^0}, \quad p^0 = -\frac{1}{\theta^0} \frac{\partial \Phi^0(\theta^0, V^0)}{\partial V^0}. \quad (1.16)$$

Since  $\theta^0$  goes to zero with increasing temperature, TRUESDELL [6] has coined the word *coldness* for the quantity  $\theta^0$ . Instead of the temperature vector  $T^i$ , it is also convenient to introduce a ‘‘coldness vector’’  $\theta^i$  by

$$\theta^i = \theta^0 V^i \quad (1.17)$$

which in the rest system has the components

$$\theta^{0i} = \delta_4^i c \theta^0 = \delta_4^i c / T^0. \quad (1.18)$$

In an arbitrary system  $S$  the fourth component  $\theta^4$  is equal to  $c$  times the reciprocal of the Planck temperature (1.7). In contrast to the  $V^i$ , which satisfies the relation

$$V_i V^i = -c^2, \quad (1.19)$$

the components  $\theta^i$  of the coldness vector are four independent variables which may replace  $T^0$  and  $\mathbf{v}$  as state variables. Thus, for a homogeneous isotropic body the thermodynamic state is completely determined by the five variables  $(\theta^i, V^0)$  or  $(\theta^i, p)$ .

The coldness vector is a time-like 4-vector with the norm

$$\theta(\theta^i) = \sqrt{-\theta_i\theta^i}/c. \quad (1.20)$$

From (1.17–19) it follows that the value of the invariant  $\theta$  is equal to the coldness,

$$\theta = \theta^0 \quad (1.21)$$

and that

$$V^i = \theta^i/\theta. \quad (1.22)$$

Thus, for given  $\theta^i$  the coldness and the four-velocity (and so  $\mathbf{v}$ ) are determined by (1.21, 22).

Now, as was shown in ref. 4, the appropriate relativistic expressions for the first and second laws of thermodynamics are the following. For an infinitesimal process we have

$$1. \text{ law: } dG_i = dI_i + dQ_i \quad (1.23)$$

$$2. \text{ law: } dS \geq -\theta^i dQ_i. \quad (1.24)$$

In (1.23)

$$dG_i = \{d\mathbf{G}, -dH/c\} \quad (1.25)$$

is the change of the four-momentum of the body

$$G_i = \{\mathbf{G}, -H/c\}, \quad (1.26)$$

and

$$dQ_i = \{d\mathbf{Q}, -dQ/c\} \quad (1.27)$$

is the four-momentum of supplied heat in the process, i.e.  $dQ$  is the heat energy and  $d\mathbf{Q}$  is the momentum conveyed to the body by the heat supply. Finally,

$$dI_i = \{d\mathbf{I}, -dA/c\} \quad (1.28)$$

is the ‘four-impulse’ of the external mechanical forces, i.e.  $d\mathbf{I}$  is the impulse or the time integral of the total mechanical force acting on the body and  $dA$  is the work performed by these forces during the process.

In non-relativistic thermodynamics the first law is expressed by one equation only, the law of conservation of energy. Due to the symmetry between momentum and energy in the theory of relativity, the first law has to be supplemented by three other equations expressing the conservation of momentum. In general neither  $G_i$ ,  $dG_i$  nor  $dI_i$  are 4-vectors, but the differences

$$dQ_i = dG_i - dI_i \quad (1.29)$$

are the covariant components of a 4-vector for any process and for an arbitrary thermodynamical system [7] [8] [9]. This important result was obtained first in the case of a fluid in ref. 7. In refs 8 and 9 the proof was given for an arbitrary thermodynamical system. For the validity of this theorem it is essential that  $dI_i$  by definition includes the impulse and the work of truly 'mechanical' forces only, i.e. the force acting on any infinitesimal part of the body, combined with the rate of work, must form a usual Minkowski four-force.

For a *reversible* process it can further be shown [7] that the four-momentum  $dQ_i^{\text{rev}}$  of supplied heat is proportional to the four-velocity, i.e.

$$dQ_i^{\text{rev}} = \frac{dQ_{\text{rev}}^0}{c^2} V_i. \quad (1.30)$$

Since  $\theta^i$  and  $dQ_i$  are 4-vectors the right hand side of (1.24) is an invariant which, on account of (1.18, 27), has the value

$$-\theta^i dQ_i = -\theta^{0i} dQ_i^0 = -\frac{cdQ_4^0}{T^0} = \frac{dQ^0}{T^0}. \quad (1.31)$$

Therefore, by (1.5), the relation (1.24) is equivalent to the relation

$$dS^0 \geq \frac{dQ^0}{T^0} \quad (1.32)$$

which is known to be valid in the rest system. Since the equality sign in (1.32) holds for reversible processes only, it follows that also in (1.24) the validity of the equality sign means that the process in question is reversible. For such processes  $dQ_i^{\text{rev}}$  is given by (1.30), which for  $i = 4$  gives

$$dQ_{\text{rev}} = dQ_{\text{rev}}^0 / \sqrt{1 - \beta^2} \quad (1.33)$$

on account of (1.12, 27). Thus, for a reversible process, (1.24) becomes

$$dS = -\theta^i dQ_i^{\text{rev}} = \frac{dQ_{\text{rev}}^0}{T^0} = \frac{dQ_{\text{rev}} \sqrt{1 - \beta^2}}{T^0} \quad (1.34)$$

by means of (1.31, 33). This may also be written in the form (1.10)

$$dS = \frac{dQ_{\text{rev}}}{T_0}, \quad (1.35)$$



where  $T_o$  is the Ott temperature (1.9). However, it should be noted that (1.24) for an *irreversible* process in general is *not* equivalent to

$$dS > \frac{dQ}{T_o}. \quad (1.35)$$

The latter relation is valid only for very special irreversible processes such as in the case of pure heat conduction.

After this short survey of the general laws of relativistic thermodynamics, we shall in the next section give the appropriate relativistic generalization of the thermodynamical potentials and of the classical relations of the type (1.16). Finally, in the last section the statistical interpretation of the relativistic potentials is given, which will allow us to calculate these quantities when the mechanical constitution of the system is known.

## 2. Relativistically Invariant Thermodynamical Potentials for Homogeneous Isotropic Bodies

The thermodynamical system considered in this section is a fluid, contained in a vessel of rest volume  $V^0$ , which exerts normal pressure only against the walls of the container. In thermal equilibrium the four-momentum of the fluid has the following components in the Lorentz system  $S$  [10]:

$$G_i = \{\mathbf{G}, -H/c\} = \{(H^0 + p^0 V^0)\gamma \mathbf{v}/c^2, -(H^0 + \beta^2 p^0 V^0) \gamma/c\} \quad (2.1)$$

where the superscript "0" refers to the rest system  $S^0$  of the fluid. The  $G_i$  are not the components of a 4-vector. Nevertheless,  $V^i G_i$  is an invariant, for we have in any system  $S$  by (1.12) and (2.1)

$$\begin{aligned} V^i G_i &= (H^0 + p^0 V^0)\gamma^2 \beta^2 - (H^0 + \beta^2 p^0 V^0)\gamma^2, \\ V^i G_i &= -H^0. \end{aligned} \quad (2.2)$$

Hence,  $-V^i G_i$  is equal to the rest energy.

Besides the four-momentum we shall consider two other quantities  $P_i$  and  $E_i$  which, in contrast to  $G_i$ , are 4-vectors. The first one is defined by

$$P_i = H^0 V_i / c^2 \quad (2.3)$$

which would be the four-momentum of the system if it were a free system. Following the terminology of LANDSBERG [11], we shall call  $P_i$  the *inclusive* four-momentum. The second 4-vector  $E_i$  is defined by

$$E_i = (H^0 + p^0 V^0) V_i / c^2. \quad (2.4)$$

A comparison with (2.1) shows that the spatial components  $E_i$  are equal to the components of the momentum  $\mathbf{G}$ . The fourth component is of the form

$$E_4 = -E/c \quad (2.5)$$

with

$$E = -cE_4 = (H^0 + p^0 V^0)\gamma = H + p^0 V^0 \gamma (1 - \beta^2)$$

or, on account of (1.4),

$$E = H + pV. \quad (2.6)$$

Hence,  $E$  is the quantity usually called enthalpy and therefore  $E_i$  will be named four-enthalpy.  $G_i$ ,  $E_i$ ,  $P_i$  are obviously related by the equations

$$\left. \begin{aligned} E_i &= P_i + p^0 V^0 V_i / c^2 \\ G_i &= E_i + \delta_{i4} pV / c. \end{aligned} \right\} \quad (2.7)$$

From (2.2–4) we get

$$V^i E_i = - (H^0 + p^0 V^0) = -E^0 \quad (2.8)$$

where  $E^0$  is the enthalpy in the rest system, and

$$V^i P_i = V^i G_i = -H^0. \quad (2.9)$$

Differentiation of the second equation (2.7) gives

$$dG_i = dE_i + \delta_{i4} d(pV) / c.$$

Therefore, the first law (1.23) may also be written in the form

$$dE_i = dJ_i + dQ_i \quad (2.10)$$

where

$$dJ_i = dI_i - \delta_{i4} d(pV) / c = \{d\mathbf{I}, -[dA + d(pV)] / c\} \quad (2.11)$$

on account of (1.28). In contrast to  $dI_i$ , the quantity  $dJ_i$  is a 4-vector. This follows at once from (2.10) since both  $dE_i$  and  $dQ_i$  are 4-vectors. Thus,  $\theta^i dJ_i$  is an invariant with the value

$$\theta^i dJ_i = \theta^{0i} dJ_i^0 = c\theta^0 dJ_4^0 = -\theta^0 [dA^0 + d(p^0 V^0)]. \quad (2.12)$$

Here we have used (1.18) and (2.11). For a reversible process the work  $dA^0$  in the rest system is

$$dA^0 = -p^0 dV^0. \quad (2.13)$$

Hence

$$\theta^i dJ_i^{\text{rev}} = -\theta^0 V^0 dp^0 = -\theta V^0 dp \quad (2.14)$$

on account of (1.4, 21).

By means of the first and second laws in the forms (2.10) and (1.24) applied to a reversible process we get

$$dS = -\theta^i dQ_i^{\text{rev}} = -\theta^i dE_i + \theta^i dJ_i^{\text{rev}}$$

or, using (2.14),

$$dS = -\theta^i dE_i - \theta V^0 dp. \quad (2.15)$$

On account of the relations (2.7) between  $E_i$ ,  $P_i$  and  $G_i$ , this equation may also be written in the alternative forms

$$dS = -\theta^i dP_i + \theta p dV^0 \quad (2.16)$$

and

$$dS = -\theta^i dG_i + \frac{\theta^4 p}{c} dV, \quad (2.17)$$

where

$$\theta^4 = \theta^0 \gamma c = \theta \gamma c \quad (2.18)$$

is the fourth component of the coldness vector. Here we have used (1.4, 12, 19), which imply

$$\theta^i V_i = -\theta c^2. \quad (2.19)$$

Now, we define two invariant state functions  $\Phi$  and  $\Psi$  by

$$\Phi \equiv -\theta^i P_i - S \quad (2.20)$$

$$\Psi \equiv -\theta^i E_i - S. \quad (2.21)$$

Since  $\theta^i$  is proportional to  $V^i$ , (2.9) shows that  $\Phi$  also may be defined as

$$\Phi = -\theta^i G_i - S. \quad (2.22)$$

On account of (2.7, 18), (1.4),  $\Phi$  and  $\Psi$  are connected by

$$\Psi = \Phi + \theta p V^0. \quad (2.23)$$

By differentiating the expressions (2.20–22) and using the appropriate forms (2.15–17) of  $dS$ , one easily finds

$$d\Phi = -P_i d\theta^i - \theta p dV^0 \quad (2.24)$$

$$d\Psi = -E_i d\theta^i + \theta V^0 dp \quad (2.25)$$

$$d\Phi = -G_i d\theta^i - \theta^4 p dV/c. \quad (2.26)$$

For a homogeneous isotropic body of the type considered here the thermal equilibrium states are determined by five independent variables. If we choose  $(\theta^i, V^0)$  as state variables, every state function appears as a function of these variables. In particular this holds for the quantity  $\Phi$ . When the function  $\Phi(\theta^i, V^0)$  is given, we can calculate five other state functions by differentiations of  $\Phi$  with respect to the five variables  $(\theta^i, V^0)$ . In fact we get from (2.24) for the inclusive four-momentum and the pressure

$$P_i = -\frac{\partial\Phi(\theta^i, V^0)}{\partial\theta^i}, \quad p = -\frac{1}{\theta} \frac{\partial\Phi(\theta^i, V^0)}{\partial V^0}. \quad (2.27)$$

Then, expressions for the remaining state functions follow from (2.7, 20). For the entropy we get for instance

$$S = -\Phi(\theta^i, V^0) + \theta^i \frac{\partial\Phi(\theta^i, V^0)}{\partial\theta^i}. \quad (2.28)$$

On the other hand, if we choose  $\theta^i$  and  $p$  as state variables we get from (2.25) the following expressions for the four-enthalpy and the rest volume

$$E_i = -\frac{\partial\Psi(\theta^i, p)}{\partial\theta^i}, \quad V^0 = \frac{1}{\theta} \frac{\partial\Psi(\theta^i, p)}{\partial p}. \quad (2.29)$$

Finally, choosing  $\theta^i$  and  $V$  as state variables, (2.26) gives for the four-momentum and the pressure

$$G_i = -\frac{\partial\Phi(\theta^i, V)}{\partial\theta^i}, \quad p = -\frac{c}{\theta^4} \frac{\partial\Phi(\theta^i, V)}{\partial V}. \quad (2.30)$$

A relativistically invariant state function which is a function of tensorial state variables can only depend on invariant combinations of these variables. The only invariant combination of the  $\theta^i$  is the norm  $\theta$  defined by (1.20). Thus, since also  $V^0$  is an invariant, the function  $\Phi(\theta^i, V^0)$  must be of the form

$$\Phi(\theta^i, V^0) = f(\theta, V^0), \quad (2.31)$$

where  $f$  is an invariant function characteristic of the material system in question. Similarly, since also  $p$  is invariant, we must have

$$\Psi(\theta^i, p) = g(\theta, p) \quad (2.32)$$

where the function  $g(\theta, p)$  is connected with  $f(\theta, V^0)$  by the relation

$$g(\theta, p) = f(\theta, V^0) + \theta p V^0 \quad (2.33)$$

following from (2.23).

Obviously, any state function which only depends on  $(\theta, V^0)$  or  $(\theta, p)$  is relativistically invariant, i.e. velocity-independent. From (2.27, 29) and (2.31, 32) we get

$$p = -\frac{1}{\theta} \frac{\partial f(\theta, V^0)}{\partial V^0}, \quad V^0 = \frac{1}{\theta} \frac{\partial g(\theta, p)}{\partial p}. \quad (2.34)$$

Thus,  $p$  and  $V^0$  are functions of  $(\theta, V^0)$  and  $(\theta, p)$ , respectively, in accordance with the invariance of these quantities. It is easily seen that also the right hand side of (2.28) is a function of  $\theta$  and  $V^0$  only, in accordance with the invariance of the entropy. For, by (2.31), (2.28) becomes

$$S = -f(\theta, V^0) + \theta^i \frac{\partial \theta}{\partial \theta^i} \frac{\partial f(\theta, V^0)}{\partial \theta} \quad (2.35)$$

and, by differentiation of  $\theta$  in (1.20) with respect to  $\theta^i$ , we get

$$\left. \begin{aligned} \frac{\partial \theta}{\partial \theta^i} &= -\theta_i / c^2 \theta \\ \theta^i \frac{\partial \theta}{\partial \theta^i} &= -\theta^i \theta_i / \theta c^2 = -\theta. \end{aligned} \right\} \quad (2.36)$$

However, as a function of the variables  $(\theta^i, V)$ ,  $\Phi(\theta^i, V)$  does not only depend on  $\theta$  and  $V$ , but also on the fourth component  $\theta^4$  of the coldness vector. In fact, since

$$V^0 = \gamma V = \frac{V\theta^4}{c\theta}, \quad (2.37)$$

we get from (2.31)

$$\Phi(\theta^i, V) = f\left(\theta, \frac{V\theta^4}{c\theta}\right). \quad (2.38)$$

By differentiating this equation with respect to  $\theta^i$  (for constant  $V$ ) and using (2.30) and (2.27) we get back the relations (2.7).

Multiplication of the equations (2.8, 9) by  $\theta = \theta^0$  gives

$$\left. \begin{aligned} \theta^i E_i &= -\theta^0(H^0 + p^0 V^0) \\ \theta^i P_i &= \theta^i G_i = -\theta^0 H^0. \end{aligned} \right\} \quad (2.39)$$

This discloses the physical meaning of the invariant functions  $\Phi$  and  $\Psi$  defined by (2.20, 21). Obviously we have

$$\Phi = \Phi^0, \quad (2.40)$$

where

$$\Phi^0 = \theta^0 H^0 - S^0 = \theta^0 F^0(\theta^0, V^0) \quad (2.41)$$

is the classical potential (1.15) obtained by multiplying the free energy of HELMHOLTZ by the coldness. Similarly we have

$$\Psi = \Psi^0 \quad (2.42)$$

where

$$\Psi^0 = \theta^0(H^0 + p^0 V^0) - S^0 = \theta^0 G^0 \quad (2.43)$$

and

$$G^0 = F^0 + p^0 V^0 \quad (2.44)$$

is the classical free energy of Gibbs.

Thus,  $\Phi$  and  $\Psi$  are the natural relativistic generalizations of the classical thermodynamic potentials — the free energies of Helmholtz and Gibbs. They have all the properties which, as mentioned in section 1, should be required of relativistic potentials. By the equations (2.27–30), all state functions are expressed in terms of partial derivatives of the potentials with respect to the variables which determine the state. In the rest system, three of the five equations (2.27) simply express the vanishing of the momentum and the two remaining equations are identical with the classical equations (1.16) which are equivalent to (1.2). In contrast to the equations (2.27–30),

which comprise the transformation properties of all thermodynamic state functions under Lorentz transformations, the Planck relations (1.8) are rather trivial transcriptions of the equation (1.2) in the rest system. In excess of (1.2), (1.8) only contains the transformation properties of  $S$ ,  $p$  and  $V$ . The function  $F(T_P, V)$  does not determine all thermodynamic properties of the system. For instance, there is no equation analogous to (1.3) by which the energy  $H$  is determined, not to speak of the components of the momentum  $\mathbf{G}$ . Thus, the free energy  $F(T_P, V)$ , as defined by (1.6), does not have all the properties of a thermodynamical potential.

From (2.31, 32) and (2.40–44) we get, since  $\theta = \theta^0$  and  $p = p^0$

$$\left. \begin{aligned} \Phi^0 &= f(\theta^0, V^0) = \theta^0 F^0(\theta^0, V^0) \\ \Psi^0 &= g(\theta^0, p^0) = \theta^0 G^0(\theta^0, p^0). \end{aligned} \right\} \quad (2.45)$$

The functions  $F^0(\theta^0, V^0)$  and  $G^0(\theta^0, p^0)$  can in principle be determined by usual thermodynamical experiments in the laboratory performed on bodies at rest. Then, by (2.45), also the functions  $f(\theta^0, V^0)$  and  $g(\theta^0, p^0)$  are known functions of the state variables, and by replacing  $\theta^0$  by  $\theta$  and  $p^0$  by  $p$  in these functions we get the expressions (2.31, 32) for the relativistic potentials  $\Phi(\theta^i, V^0)$ ,  $\Psi(\theta^i, p)$ . Also the function  $\Phi(\theta^i, V)$  of the variables  $(\theta^i, V)$  is then determined by (2.38) and, by means of (2.27–30), we can calculate all thermodynamical state functions in an arbitrary system of inertia.

### 3. Statistical Interpretation of the Relativistic Potentials

Historically, statistical mechanics was developed with the aim to provide a ‘rational explanation’ of the thermodynamic laws and thereby obtaining a means of calculating the thermodynamical state functions from the knowledge of the mechanical structure of the system in question. In non-relativistic mechanics the statistical methods developed by GIBBS supplied the most general solution of this problem. In the paper quoted in reference [4], a relativistic generalization of Gibbs’ classical theory was given which, as we shall see now, supplies an immediate interpretation of the relativistic thermodynamical potentials introduced in section 2.

Consider a system consisting of  $n$  particles of proper mass  $m$  which, in a certain system of inertia  $S^0$ , are acted upon by forces derivable from a timeindependent mechanical potential

$$U_g^0(\mathbf{x}_1^0, \dots, \mathbf{x}_r^0, \dots, \mathbf{x}_n^0, a_l). \quad (3.1)$$

Here, the  $a_l$  are invariant parameters describing the configurations of the external systems which may influence our system.  $U_g^0$  will contain the interaction  $U^0(\mathbf{x}_r^0, a_l)$  of the separate particles with outside systems (for instance the walls of a container) as well as the interaction  $W^0(\mathbf{x}_1^0, \dots, \mathbf{x}_n^0)$  between the particles. Thus, we assume that the forces acting on the particles are derivable from a potential of the form

$$U_g^0 = \sum_{r=1}^n U^0(\mathbf{x}_r^0, a_l) + W^0(\mathbf{x}_1^0, \dots, \mathbf{x}_n^0). \quad (3.2)$$

This assumption restricts somewhat the applicability of the theory, for in relativity theory it is generally not possible to describe the interaction between the particles in this simple way. In general the interaction has to be described by an intermediary field which has to be treated as a separate physical system with an infinite number of degrees of freedom. However, for a gas of particles of nucleonic mass, the relation

$$\frac{kT^0}{mc^2} \ll 1, \quad (k = \text{Boltzmann's constant}) \quad (3.3)$$

is very well satisfied, which means that the system may be treated non-relativistically in  $S^0$ . In fact, if  $m$  is the mass of a nucleon, the proper temperature  $T^0$  would have to be of the order of  $10^{13}$  °K in order to make the left hand side of (3.3) of order unity and, as far as we know, temperatures of this order of magnitude are reached nowhere in our present universe. A violation of the condition (3.3) will occur only for electrons under very special circumstances. Excluding these rare cases from our consideration, it has a good meaning to describe the interaction in  $S^0$  by a potential of the form (3.2). As regards the mutual interaction of the particles the treatment is then only approximate (although in practically all cases an extremely good approximation), but for a system of non-interacting particles, where  $W^0 = 0$ , the detailed treatment given in reference [4] is exact.

In the following development, the potential  $U^0$  will be regarded as an invariant scalar which means that we, in any Lorentz system  $S$ , introduce a function  $U_g(x^i, \dots, x^i)$  of the space-time coordinates of the particles defined by

$$U_g(x_1^i, \dots, x_r^i, \dots, x_n^i, a) = U_g^0(\mathbf{x}_1^0, \dots, \mathbf{x}_r^0, \dots, \mathbf{x}_n^0, a), \quad (3.4)$$

where  $x_r^i = \{x_r, ct_r\}$  and  $\mathbf{x}_r^0$  are connected by the Lorentz transformation leading from  $S^0$  to  $S$ . Thus,  $U_g$  is obtained from  $U_g^0$  by eliminating the



arguments  $\mathbf{x}_r^0$  in the latter function by means of the Lorentz transformation. If we put all the time-coordinates equal to  $t$  in this function,

$$t_1 = t_2 = \dots = t_n = t, \tag{3.5}$$

we arrive at a definite function of the space-coordinates  $\mathbf{x}_r$  and the time variable  $t$ :

$$U_g(\mathbf{x}_1, \dots, \mathbf{x}_r, \dots, \mathbf{x}_n, t, a). \tag{3.6}$$

This function will of course depend on the external parameters ( $a$ ), but it will obviously also depend on the parameters of the Lorentz transformation, in particular on the relative velocity  $v$  of  $S^0$  and  $S$ . Thus, for a special Lorentz transformation, where

$$\mathbf{x}_r^0 = \gamma(\mathbf{x}_r - vt_r), y_r^0 = y_r, z_r^0 = z_r, \tag{3.7}$$

the function (3.6) is

$$U_g(\dots, x_r, y_r, z_r, \dots, t, a) = U_g^0(\dots, \gamma(x_r - vt), y_r, z_r, \dots, a). \tag{3.8}$$

Now let us assume that our system (the gas of  $n$  particles) is in a state of thermodynamical equilibrium which in a Lorentz system  $S$  is described by the state variables  $(\theta^i, a)$ . In this situation we do not have a precise knowledge of the *mechanical* state, which is defined by the  $6n$  'coordinates'

$$(\xi_{\mu}) = (\mathbf{p}_1, \mathbf{x}_1, \dots, \mathbf{p}_r, \mathbf{x}_r, \dots, \mathbf{p}_n, \mathbf{x}_n) \tag{3.9}$$

of the points in the phase space  $\Sigma(S)$  of the system in  $S$ . According to the developments in reference [4], the situation in question is statistically described by the following 'canonical' probability density  $\mathfrak{P}(\xi_{\mu})$  in  $\Sigma(S)$ :

$$\left. \begin{aligned} \mathfrak{P}(\xi) &= \exp\{(\Phi + \theta^i P_i^g(\xi, a))/k\} \\ P_i^g &= \sum_{r=1}^n p_r^i + U_g(\mathbf{x}_1, \dots, \mathbf{x}_r, \dots, \mathbf{x}_n, t, a) V_i/c^2 \end{aligned} \right\} \tag{3.10}$$

(cf. Eqs. (4; 7.1, 2) in section 7 of reference [4]). In (3.10),  $p_r^i = \{\mathbf{p}_r, -E_r/c\}$  is the 'bare' four-momentum of the  $r$ 'th particle,  $V_i$  is the four-velocity of  $S^0$  relative to  $S$ , and the quantity  $\Phi$  is defined by

$$\left. \begin{aligned} \int \cdots \int \mathfrak{P}(\xi) d\xi &= 1, \\ d\xi &= \prod_{\mu=1}^{6n} d\xi_{\mu}, \end{aligned} \right\} \quad (3.11)$$

or

$$\exp\{-\Phi(\theta^i, a)/k\} = \int \cdots \int \exp\{\theta^i P_i^g(\xi, a)/k\} d\xi. \quad (3.12)$$

A comparison of (2.22) with (4; 5.38) in reference [4] shows that the statistical quantity  $\Phi$  in (3.10) may be identified with the relativistic thermodynamic potential introduced in section 2 of the present paper.

In the 'rest' system  $S^0$ , (3.10) reduces to the canonical distribution of GIBBS

$$\mathfrak{P}^0 = \exp\{(\Phi^0 - \theta^0 \check{\xi}_g^0)/k\}, \quad (3.13)$$

where

$$\Phi^0 = \Phi,$$

and

$$\check{\xi}_g^0 = \sum_{r=1}^n E_r^0 + U_g^0 \quad (3.14)$$

is the Hamiltonian in  $S^0$ . Further, in  $S^0$  the equation (3.12) becomes

$$\exp\{-\Phi^0(\theta^0, a)/k\} = \int \cdots \int \exp\{-\theta^0 \check{\xi}_g^0/k\} d\xi^0, \quad (3.15)$$

which in the usual way gives us  $\Phi^0(\theta^0, a)$  as a function of  $(\theta^0, a)$ .

In section 7 of reference [4] we have calculated the functions  $\Phi$  and  $\Phi^0$  in (3.12, 15). According to (4; 7,53, 54, 33, 35, 41) we have

$$\Phi(\theta^i, a) = f(\theta, a), \quad \Phi^0(\theta^0, a) = f(\theta^0, a), \quad (3.16)$$

where  $f(\theta, a)$  is a function of the norm  $\theta$  and  $(a)$ , defined by

$$f(\theta, a) = f_p(\theta) + f_q(\theta, a), \quad (3.17)$$

$$\left. \begin{aligned} \exp\{-f_p(\theta)/k\} &= \int \cdots \int \exp\{-\theta \sum_r E_r^0/k\} d\mathbf{p}_1^0 \cdots d\mathbf{p}_n^0 \\ &= \left[ \int \exp\{-\theta E^0/k\} d\mathbf{p}^0 \right]^n = \left[ \frac{2\pi^2 m^2 c k}{i\theta} H_2^{(1)}(imc^2\theta/k) \right]^n, \end{aligned} \right\} \quad (3.18)$$

$$\exp\{-f_q(\theta, a)/k\} = \int \cdots \int \exp\{-\theta U_g^0(\mathbf{x}_1^0, \dots, \mathbf{x}_n^0, a)/k\} d\mathbf{x}_1^0 \cdots d\mathbf{x}_n^0. \quad (3.19)$$

For non-interacting particles the latter expression reduces to the  $n$ 'th power of the expression (4; 7.41). In the case considered here, where (3.3) holds, the argument in the Hankel function in (3.18) is very large and we can substitute this function by its asymptotical expansion. Then (3.18) becomes

$$\exp\{-f_p(\theta)/k\} = \frac{2\pi mk}{\theta} \exp\{-nmc^2\theta/k\} \quad (3.20)$$

in accordance with the corresponding formula in non-relativistic statistical mechanics. From (4; 7.56, 57) we get

$$P_i \equiv -\frac{\partial\Phi(\theta^i, a)}{\partial\theta^i} = \frac{\langle \hat{\mathfrak{S}}_g^0 \rangle^0}{c^2} V_i \quad (3.21)$$

which is the statistical expression for the inclusive four-momentum of the system defined by (2.3).

We shall now in particular consider the case where the interaction between the particles and the walls of a container are the only external forces on the particles. Then,  $U^0(\mathbf{x}_r^0, a)$  is zero inside the container and increases rapidly to a very high value when the particles approach the walls. Let us for simplicity assume that the container has the form of a cylinder with the axis lying in the direction of the  $x^0$ -axis of the system  $S^0$  and with the endwalls placed at  $x^0 = 0$  and  $x^0 = l^0$ , respectively. If the latter wall is a movable piston we may change the volume  $V^0$  by moving the piston i.e. by changing  $l^0$ , for we have

$$V^0 = F^0 l^0 \quad (3.22)$$

where  $F^0$  is the (constant) area of the endwalls. With this arrangement the only way in which the system (the gas) can be influenced *mechanically* by the external world is by changing the position of the piston. Thus, in this case there is only one external parameter  $a$  for which we can choose  $l^0$  or  $V^0$  and

$$f_q(\theta, a) = f_q(\theta, l^0) = f_q(\theta, V^0) \quad (3.23)$$

is a function of  $\theta$  and  $l^0$  or  $V^0$ . For non-interacting particles, where  $W^0 = 0$  and  $U^0(\mathbf{x}_r^0, a)$  has the property mentioned above, we get from (3.19)

$$\begin{aligned}\exp\{-f_q/k\} &= (F^0 l^0)^n = V^{0n} \\ f_q &= -kn \ln(F^0 l^0) = kn \ln V^0.\end{aligned}$$

Thus, for an ideal gas  $f_q$  is a function of  $l^0$  or  $V^0$  only, but for interacting particles  $f_q$  (and  $f$ ) will in general depend on both  $\theta$  and  $V^0$ . Therefore, in our case, (3.16) gives

$$\Phi(\theta^i, V^0) = f(\theta, V^0), \quad \Phi^0(\theta^0, V^0) = f(\theta^0, V^0) \quad (3.24)$$

and the equations (3.21) become identical with four of the thermodynamical equations (2.27). Further, if we identify the mean value of the force  $p$  per unit area exerted by the piston on the fluid with the thermodynamic pressure  $p$ , we get from (4; 7.15)

$$\left. \begin{aligned} p = \langle p \rangle &= -\frac{1}{\theta} \frac{\partial \Phi(\theta^i, V^0)}{\partial V^0} = -\frac{1}{\theta} \frac{\partial f(\theta, V^0)}{\partial V^0}, \\ p^0 = \langle p^0 \rangle^0 &= -\frac{1}{\theta^0} \frac{\partial f(\theta^0, V^0)}{\partial V^0} = -\frac{1}{\theta^0} \frac{\partial \Phi^0(\theta^0, V^0)}{\partial V^0}, \end{aligned} \right\} \quad (3.25)$$

in accordance with the last equations (2.27) and (1.16). This identification is justified, since the ratio of the fluctuation to the mean value of the piston force is proportional to  $n^{-1/2}$  and therefore generally speaking extremely small for a ponderable amount of matter, where  $n$  is of the order of Avogadro's number. In the rest system the equations (3.21) reduce to the single equation

$$\langle \delta_g^0 \rangle^0 = \frac{\partial f(\theta^0, V^0)}{\partial \theta^0} = \frac{\partial \Phi^0(\theta^0, V^0)}{\partial \theta^0}. \quad (3.26)$$

The statistical mean value equations (3.21, 25, 26) are in complete agreement with the thermodynamic equations (2.27) and (1.16).

Thus, relativistic statistical mechanics provides an immediate interpretation of the thermodynamic potential  $\Phi$  and the relations (2.27) and, by means of (3.12) (with  $a = V^0$ ), we are now also able to calculate  $\Phi = f(\theta, V^0)$  when the mechanical potential  $U_g$  is given. However, in accordance with the remarks at the end of section 2, it is not necessary to perform the calculation of  $\Phi$  in the general system  $S$  for, by (3.16–19), the function  $f$  is already completely determined by the equation (3.15) holding in the rest system  $S^0$ .

Now we turn to the question of the statistical mechanical interpretation of the relativistic potential  $\Psi(\theta^i, p)$  introduced in (2.21). Just as in the case

of  $\Phi$  it is sufficient to give an interpretation of the function  $\Psi^0(\theta^0, p^0)$  in the rest system. In the preceding considerations it was found that  $\Phi(\theta^i, V^0)$  appears as an essential quantity in the canonical distribution (3.10) corresponding to a situation where the thermodynamical variables  $\theta^i$  and  $V^0$  have well-defined values. In  $S^0$  this means that the piston is fixed in a definite position at  $x^0 = l^0$  and that the gas has been brought in thermal contact with a heat reservoir of coldness  $\theta^0$ . *Thermodynamically*, fixed values of  $\theta^0$  and  $V^0$  correspond to definite values of  $H^0$  and  $p^0$  for the energy and the pressure as given by the equations of state, for instance in the form (1.16). Therefore, we can eliminate  $V^0$  and define the state by  $(\theta^0, p^0)$  instead of by  $(\theta^0, V^0)$  and the potential  $\Psi^0$  is then given by the relation (2.23), i.e.

$$\Psi^0 = \Phi^0 + \theta^0 p^0 V^0 . \quad (3.27)$$

However, in the statistical mechanical description, fixed values of  $\theta^0$  and  $V^0$  do *not* correspond to exactly defined values for the energy and the pressure and the thermodynamical equations of state are valid only for the *mean values* of the energy and the external force. As often emphasized by NIELS BOHR [12], this circumstance constitutes an instructive example of complementarity in classical physics. Energy and pressure are complementary to temperature and volume, respectively, in much the same way as momentum and position of a particle in quantum mechanics. It is true that, for systems of ponderable size where  $n$  is very large, the complementary character of the mentioned quantities is usually not apparent, but in principle, and in special cases also in praxis, the recognition of this complementarity is of importance for the understanding of the properties of thermodynamical systems.

As in quantum mechanics, the complementarity of the mentioned thermodynamical quantities is due to the fact that the experimental arrangements which allow the fixation of definite values for the quantities in question are mutually exclusive. For instance, in order to give definite values to the coldness  $\theta^0$  and the volume  $V^0$  we have, as already mentioned, to bring the gas in thermal contact with a large heat reservoir for a sufficiently long time during which the piston is fastened in a fixed position. When thermal equilibrium is reached, any previous knowledge of the energy and the piston force will be lost, and our knowledge of the mechanical state of the system after this procedure is adequately described by the canonical distribution (3.13, 15) with  $a = V^0$ , according to which the thermodynamical relations (1.16) are valid for the *mean values* of the energy and pressure only.

On the other hand, if we want to assure definite values for the coldness  $\theta^0$  and the *pressure*  $p^0$ , we have to *unfasten* the piston and subject it to a constant external force

$$K_p^0 = F^0 p^0 \quad (3.28)$$

instead of keeping it in a fixed position. After thermal equilibrium is reached, this situation is again adequately described by a canonical distribution (3.13, 15) but now applied to the system  $(g+p)$  consisting of the gas plus the piston. The latter can be treated as a particle of macroscopical mass  $M$  which can move freely along the  $x^0$ -axis. Thus, if  $n$  is the number of degrees of freedom of the gas, the corresponding number for the system  $(g+p)$  is  $n+1$ , and the coordinate  $l^0$  of the piston and the volume  $V^0$  given by (3.22) do not have exactly defined values in this situation. The constant external force (3.28) is derivable from a potential  $U_p^0$ :

$$K_p^0 = - \frac{\partial U_p^0(l^0, p^0)}{\partial l^0}$$

with

$$U_p^0(l^0, p^0) = K_p^0 l^0 = p^0 F^0 l^0 = p^0 V^0 \equiv U_p^0(V^0, p^0), \quad (3.29)$$

and as external parameter  $a$  for the system  $(g+p)$  we may choose the pressure  $p^0$ .

If we use  $V^0$  instead of  $l^0$  as 'generalized' coordinate of the piston, its (non-relativistic) kinetic energy is

$$T_p^0 = M \dot{V}^{02} / 2F^{02} = \quad , \quad \dot{V}^0 = \frac{dV^0}{dt^0}. \quad (3.30)$$

The corresponding canonical momentum is

$$p_p^0 = \frac{dT_p^0}{d\dot{V}^0} = M \dot{V}^0 / F^{02}. \quad (3.31)$$

Now, the mechanical potential of the system gas + piston is

$$U_{(g+p)}^0 = U_g^0(\mathbf{x}_1^0, \dots, \mathbf{x}_u^0, V^0) + U_p^0(V^0, p^0) \quad (3.32)$$

and its Hamiltonian (disregarding the rest energy of the piston)

$$\xi_{(g+p)}^0 = \xi_g^0 + p^0 V^0 + F^{02} p_p^{02} / 2M. \quad (3.33)$$

Thus, the probability density (3.13) of the system  $(g+p)$  is

$$\mathfrak{P}_{(g+p)}^0 = \exp\{(\Phi_{(g+p)}^0 - \theta^0 \xi_{(g+p)}^0)/k\}. \quad (3.34)$$

It is a function of the phase-coordinates  $(\xi^0)$  of the gas and the canonical variables  $p_p^0$  and  $V^0$  of the piston, and  $\Phi_{(g+p)}^0$  is determined by the equation

$$\int \cdot \int \mathfrak{P}_{(g+p)}^0 d\xi^0 dp_p^0 dV^0 = 1. \quad (3.35)$$

We may now calculate the mean values of quantities referring to the gas and the piston. According to the equipartition theorem, the mean value of the kinetic energy of the piston is  $kT^0$  and the velocity of the piston will be of the order  $v_p \sim (kT^0/M)^{1/2}$ . For  $M$  of the order of a gram,  $v_p$  is therefore extremely small which means that the piston will practically always be found at rest in spite of its being unfastened. By integration of (3.34) over  $p_p^0$  from  $-\infty$  to  $+\infty$  we get the probability density  $\mathfrak{P}^*(\xi^0, V^0)$  of finding the gas at a point  $(\xi^0)$  in its phase space and with a volume  $V^0$ , irrespective of the momentum of the piston. Obviously  $\mathfrak{P}^*$  is of the form

$$\mathfrak{P}^* = \exp\{(\Psi^0 - \theta^0 \xi_{\zeta}^*)/k\}, \quad (3.36)$$

where

$$\xi_{\zeta}^* = \xi_g^0(\xi^0, V^0) + p^0 V^0 \quad (3.37)$$

and  $\Psi^0$  is a function of  $\theta^0$  and  $p^0$  given by

$$\int \cdot \int \mathfrak{P}^* d\xi^0 dV^0 = \iint \exp\{(\Psi^0 - \theta^0 \xi_{\zeta}^*(\xi^0, V^0, p^0))/k\} d\xi^0 dV^0 = 1. \quad (3.38)$$

Further integration of  $\mathfrak{P}^*$  over  $(\xi^0)$  gives us the probability density  $W(V^0)$  for the gas having the volume  $V^0$ . By means of (3.36, 37) and (3.15) (with  $\alpha = V^0$ ), we get

$$W(V^0) = \exp\{(\Psi^0 - \Phi(\theta^0, V^0) - \theta^0 p^0 V^0)/k\}, \quad (3.39)$$

$$\int_0^{\infty} W(V^0) dV^0 = \int_0^{\infty} \exp\{\Psi^0(\theta^0, p^0) - \Phi(\theta^0, V^0) - \theta^0 p^0 V^0/k\} dV^0 = 1. \quad (3.40)$$

The latter equation may also be written

$$\exp\{-\Psi^0/k\} = \int_0^{\infty} \exp\{-(\Phi(\theta^0, V^0) + \theta^0 p^0 V^0)/k\} dV^0, \quad (3.41)$$

which allows to calculate  $\Psi^0(\theta^0, p^0)$  when the function  $\Phi^0(\theta^0, V^0)$  in (3.24) is known. The most probable value  $\bar{V}^0$  of  $V^0$  is determined by the equation

$$\left. \begin{aligned} \text{i.e.} \quad \frac{dW(V^0)}{dV^0} &= -W(V^0) \left( \frac{\partial \Phi(\theta^0, V^0)}{\partial V^0} + \theta^0 p^0 \right) / k = 0, \\ \frac{\partial \Phi(\theta^0, \bar{V}^0)}{\partial \bar{V}^0} + \theta^0 p^0 &= 0. \end{aligned} \right\} \quad (3.42)$$

By partial differentiation of (3.40) with respect to  $\theta^0$ , we get in the usual way

$$\left. \begin{aligned} \int_0^\infty \left( \frac{\partial \Psi^0(\theta^0, p^0)}{\partial \theta^0} - \frac{\partial \Phi(\theta^0, V^0)}{\partial \theta^0} - p^0 V^0 \right) W(V^0) dV^0 &= 0 \\ \text{or} \quad \frac{\partial \Psi^0(\theta^0, p^0)}{\partial \theta^0} &= \langle \frac{\partial \Phi(\theta^0, V^0)}{\partial \theta^0} \rangle_0 + p^0 \langle V^0 \rangle_0. \end{aligned} \right\} \quad (3.43)$$

Further, by differentiations of (3.40) with respect to  $p^0$ ,

$$\langle V^0 \rangle_0 = \frac{1}{\theta^0} \frac{\partial \Psi^0(\theta^0, p^0)}{\partial p^0}, \quad (3.44)$$

$$\sigma^2\{V^0\} \equiv \langle (V^0 - \langle V^0 \rangle_0)^2 \rangle_0 = -\frac{k}{\theta^{02}} \frac{\partial^2 \Psi^0(\theta^0, p^0)}{\partial p^{02}} = -\frac{k}{\theta^0} \frac{\partial \langle V^0 \rangle_0}{\partial p^0}, \quad (3.45)$$

where  $\sigma^2\{V^0\}$  is the square of the fluctuation of the volume around its mean value  $\langle V^0 \rangle_0$ . Since both  $\langle V^0 \rangle_0$  and  $\sigma^2\{V^0\}$  are proportional to  $n$ , the ratio  $R$  of the fluctuation to the mean value of  $V^0$  is proportional to  $n^{-1/2}$ :

$$R(\theta^0, p^0) = \frac{\sigma\{V^0\}}{\langle V^0 \rangle_0} = O(n^{-1/2}). \quad (3.46)$$

Apart from very special cases where  $\frac{\partial \langle V^0 \rangle_0}{\partial p^0}$  is exceptionally large (like at transitions from one phase of the gas to another), the fluctuation of  $V^0$  is completely negligible for a ponderable amount of gas where  $n$  is of the order of Avogadro's number. Therefore, in such cases  $\langle V^0 \rangle_0$  may be identified with the thermodynamical variable  $V^0$ , and the relation (3.44) between



volume, coldness, and pressure must be identical with the relation (3.25). Moreover, the most probable volume  $\bar{V}^0$  given by (3.42) must be equal to the mean value in this case, i.e.

$$\bar{V}^0 = \langle V^0 \rangle^0, \quad (3.47)$$

in accordance with the result of a comparison of (3.42) with (3.25). This means that the function (3.39) (for fixed  $\theta^0$  and  $p^0$ ) must have a very steep maximum at  $V = \bar{V}^0 = \langle V^0 \rangle^0$  with a mean breadth equal to  $R(\theta^0, p^0)$ . Thus the integral in (3.40) becomes equal to the maximum value  $W(\bar{V}^0)$  times  $R$ , and we get from (3.40)

$$R(\theta^0, p^0) \exp\{(\Psi^0(\theta^0, p^0) - \Phi(\theta^0, \bar{V}^0) - \theta^0 p^0 \bar{V}^0)/k\} = 1 \quad (3.48)$$

or

$$\Psi^0(\theta^0, p^0) = \Phi(\theta^0, \bar{V}^0) + \theta^0 p^0 \bar{V}^0 - k \ln R. \quad (3.49)$$

Since  $\Psi^0$ ,  $\Phi^0$  and  $\bar{V}^0$  are proportional to  $n$  while  $\ln R$  only contains the logarithm of  $n$ , we may neglect the last term in (3.49) in the case of large  $n$  where (3.47) holds.

Hence

$$\Psi^0(\theta^0, p^0) = \Phi^0(\theta^0, \langle V^0 \rangle^0) + \theta^0 p^0 \langle V^0 \rangle^0. \quad (3.50)$$

A comparison of this equation with the thermodynamical relation (3.27) shows that the statistical quantity  $\Psi^0$  entering in (3.36) may be identified with the thermodynamical potential  $\Psi^0(\theta^0, p^0)$ .

The quantity  $\xi^*$  defined by (3.37) is equal to the energy of the gas plus the potential energy (3.29) of the piston in the external field. By partial differentiation of (3.38) with respect to  $\theta^0$  we get for the mean value of  $H^*$

$$\langle \xi^* \rangle = \frac{\partial \Psi^0(\theta^0, p^0)}{\partial \theta^0} = \left\langle \frac{\partial \Phi^0(\theta^0, V^0)}{\partial \theta^0} \right\rangle^0 + p^0 \langle V^0 \rangle^0 \quad (3.51)$$

on account of (3.43). According to (3.26),  $\frac{\partial \Phi^0(\theta^0, V^0)}{\partial \theta^0}$  is the mean value of the energy  $\xi_g^0$  of the gas in a canonical ensemble with a fixed value  $V^0$  of the volume. Hence,  $\left\langle \frac{\partial \Phi^0(\theta^0, V^0)}{\partial \theta^0} \right\rangle^0$  is the mean value of  $H_g^0$  in the ensemble with varying  $V^0$  described by (3.34). This is in accordance with the relation obtained by taking the mean value of the equation (3.37) over the ensemble (3.34)

$$\langle \xi^* \rangle^0 = \langle \xi_g^0 \rangle^0 + p^0 \langle V^0 \rangle^0. \quad (3.52)$$

The equations (3.51, 52) are exact for all  $n$ . However, for large  $n$ , where the function  $W(V^0)$  has a steep maximum and (3.47) holds, (3.51) becomes

$$\langle \xi^* \rangle^0 = \frac{\partial \Phi^0(\theta^0, \bar{V}^0)}{\partial \theta^0} + p^0 \bar{V}^0. \quad (3.53)$$

A comparison with the first equation (1.16) shows that the first term on the right hand side of (3.53) must be identified with the thermodynamical energy  $H^0$  of the gas and, taking account of (2.8), we come to the conclusion that  $\langle \xi^* \rangle^0$  in (3.51, 53) must be the statistical analogue of the thermodynamical enthalpy  $E^0$  of the gas in the rest system. The (exact) mean value equations (3.44, 51) are obviously the statistical analogues of the thermodynamical relations (2.29) which, in the rest system  $S^0$ , reduce to the two equations

$$V^0 = \frac{1}{\theta^0} \frac{\partial \Psi^0(\theta^0, p^0)}{\partial p^0}, \quad E^0 = \frac{\partial \Psi^0(\theta^0, p^0)}{\partial \theta^0}. \quad (3.54)$$

Thus, the statistical quantity  $\Psi^0$  given by (3.38) or (3.40) has all the properties of the thermodynamical potential  $\Psi^0$ . It is closely connected with the  $\Phi^0$ -function for the system gas + piston (if we disregard the rest energy of the piston). From the definitions (3.38, 35) of  $\Psi^0$  and  $\Phi_{(g+p)}^0$  one easily finds

$$\Phi_{(g+p)}^0 = \Psi^0 - k \ln \frac{\sqrt{2\pi Mk/\theta^0}}{F^0}. \quad (3.55)$$

Since  $\Phi^0$  and  $\Psi^0$  are proportional to  $n$ , we may neglect the last term on the right side of this equation for a ponderable amount of gas. Thus, for large  $n$ ,

$$\Phi_{(g+p)}^0(\theta^0, p^0) = \Psi^0(\theta^0, p^0). \quad (3.55)$$

In an arbitrary system  $S$ , the corresponding potential  $\Psi(\theta^i, p)$  is obtained from  $\Psi^0(\theta^0, p^0)$  by replacing  $\theta^0$  and  $p^0$  by the norm  $\theta$  and  $p$ , respectively. These considerations lead to the following physical interpretation of the four-enthalpy  $E_i$  in an arbitrary system  $S$ . *The quantities  $E_i$ , as defined by (2.4) or (2.29), are equal to the components of the inclusive four-momentum of the system  $(g+p)$  minus  $MV_i$  where  $M$  is the proper mass of the piston.*

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