A Relativistic Form of Statistical Thermodynamics

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1. Introduction

In a recent paper (Georgiou, 1968) we have shown, from a classical thermodynamical and also from a statistical mechanical viewpoint, that the only consistent scheme of Lorentz transformations of thermodynamical variables is as follows

$$E = \gamma(\nu) \left(E^{0} + \frac{\nu^{2}}{c^{2}} p^{0} V^{0} \right)$$
 (1.1)

$$p = -\gamma(\nu) \, \nu(E^0 + p^0 \, V^0) \tag{1.2}$$

$$p = p^0 \tag{1.3}$$

$$V = V^0 / \gamma(\nu) \tag{1.4}$$

$$T = \gamma(\nu) T^0 \tag{1.5}$$

$$Q = \gamma(\nu) Q^0 \tag{1.6}$$

$$S = S^0 \tag{1.7}$$

where E, p, p, V, T, Q and S are the energy, momentum, pressure, volume, temperature, heat and entropy of the system in an inertial frame σ ; $\gamma(\nu)$ is the Lorentz factor $(1 - \nu^2/c^2)^{-1/2}$, and the superscript zero refers to the measures of these quantities in the rest-frame σ^0 of the system, the velocity of σ in σ^0 being ($\nu, 0, 0$). The transformations of the temperature and heat are the Ott-Arzelies (Ott, 1963; Arzelies, 1965) formulae, which have replaced the corresponding Planck-Einstein formulae.

In the aforementioned paper (Georgiou, 1968) some statistical mechanical notions were used, but no formalism was developed. In the present work, a résumé of a possible relativistic statistical thermodynamical formalism is given, using 'sums over states'. Another formalism is also possible, using 'integrations over phase-space', but this formalism is only briefly pointed out. It is hoped that this work is of interest to physicists because it gives a relativistic formulation of statistical thermodynamics, and it indicates the modifications resulting from relativistic considerations. Furthermore, it

A. GEORGIOU

correlates correctly measurements of any thermodynamical quantity made by different inertial observers, by showing that the transformations (1.1)to (1.7) are the only possible transformations allowed by the statistical mechanics of the system.

2. Sums over States

Consider an assembly of N identical atoms in loose energy contact, in an enclosure of proper volume V^0 . The problem is the distribution of a given amount of energy E and a given amount of momentum p over the N atoms, subject to the conditions

$$\sum \bar{a}_i = N, \qquad \sum \bar{a}_i \epsilon_i = E, \qquad \sum \bar{a}_i p_i = p$$
 (2.1)

where \bar{a}_i is the time-average of the occupation number of the *i*th eigenstate, given by

$$\bar{a}_i = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} a_i(t) \, dt_i \tag{2.2}$$

 a_i being the instantaneous occupation number of this eigenstate. We want to maximize $\ln(N!/a_1^{0}!a_2^{0}!,...,a_i^{0}!,...)$ subject to the conditions (2.1) in σ^0 . These considerations, together with the fact that $a_i = a_i^{0} = \bar{a}_i^{0}$ give

$$\bar{a}_i = \left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_i^0}{c^2}\right) \bar{a}_i^0 = \left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_i^0}{c^2}\right) \exp\left(-\lambda - \theta_\mu p_i^\mu\right)$$
(2.3)

where θ_{μ} is a 4-vector given by $\theta_{\mu} = \gamma(\nu)(\nu, 0, 0, c)\phi$, λ and ϕ are invariant scalar functions and p_i^{μ} is the 4-momentum of a particle in the *i*th eigenstate; the product $\theta_{\mu}p_i^{\mu}$ has, of course, the invariant value $\phi \epsilon_i^0$. Thus, if l^0 and l are the measures in σ^0 and σ of a particular quantity of the system, then

$$l^{0} = \sum \bar{a}_{i}^{0} l_{i}^{0}, \qquad l = \sum \bar{a}_{i} l_{i}, \qquad (2.4)$$

where l_i^0 and l_i are the instantaneous contributions to this quantity of particles in the *i*th eigenstate in σ^0 and σ , respectively.

Inducing a variation to the parameters θ_{μ} and λ , we obtain

$$\delta\{\theta_{\mu} \sum \bar{a}_{i} p_{i}^{\mu} + NF\} = \theta_{\mu} \sum (\delta \bar{a}_{i}) p_{i}^{\mu}$$
(2.5)

where the invariant function F is given by

$$F = \ln e^{\lambda} \sum_{i} \tilde{a}_{i} = \ln \sum_{i} \left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_{i}^{0}}{c^{2}} \right) \exp\left(-\theta_{\mu} p_{i}^{\mu}\right) = F^{0}$$
(2.6)

The invariant equation (2.5) holds in any inertial system, and it is easy to show that it is equivalent to

$$\delta\{\phi \sum \bar{a}_i^0 \epsilon_i^0 + NF\} = \phi \sum (\delta \bar{a}_i^0) \epsilon_i^0$$
(2.7)

where

$$\sum \left(\delta \tilde{a}_i^{0}\right) \epsilon_i^{0} = \delta Q^0, \qquad \sum \tilde{a}_i^{0} \epsilon_i^{0} = E^0$$
(2.8)

are the heat (absorbed) and energy of the system, respectively, in σ^0 . Thus if k is the Boltzmann constant, the temperature T^0 in σ^0 is

$$T^0 = 1/k\phi \tag{2.9}$$

and the entropy is

$$S = \frac{1}{T^0} \sum \bar{a_i}^0 \epsilon_i^0 + kN \ln \sum \exp(-\phi \epsilon_i^0)$$
 (2.10)

It may be shown that the heat in σ is

$$\delta Q = \gamma(\nu) \,\delta Q^0 \tag{2.11}$$

and that $\sum \bar{a_i} p_i^{\mu}$ is not a 4-vector; we have

$$\sum \tilde{a}_i p_i^{\mu} = (\boldsymbol{p}, E/c) \tag{2.12}$$

where

$$\boldsymbol{p} = -\gamma(\nu) \frac{\boldsymbol{\nu}}{c^2} \sum \bar{a_i}^0 (\epsilon_i^0 + c^2 p_i^{02} / 3\epsilon_i^0) = -\gamma(\nu) \frac{\boldsymbol{\nu}}{c^2} (E^0 + p^0 V^0) \quad (2.13)$$

$$E = \gamma(\nu) \sum \bar{a}_i^{\ 0} (\epsilon_i^{\ 0} + \nu^2 p_i^{\ 02} / 3\epsilon_i^{\ 0}) = \gamma(\nu) \left(E^0 + \frac{\nu^2}{c^2} p^0 V^0 \right)$$
(2.14)

are the average 3-momentum and energy in σ . Thus the integrating factor of the heat is $\phi/\gamma(\nu)$, and so the temperature T in σ is

$$T = \gamma(\nu) T^0 \tag{2.15}$$

Referring to equation (2.5), θ_{μ} is an integrating factor of $\sum (\delta \tilde{a}_i) p_i^{\mu}$ and this defines the 4-vector temperature

$$T_{\mu} = \frac{c^2 \theta_{\mu}}{k \theta_{\mu} \theta^{\mu}} = \gamma(\nu) (\mathbf{v}, c) T^0$$
(2.16)

In terms of T_{μ} , equation (2.5) may be written as

$$\delta\left\{k^{2} \phi^{2} T_{\mu} \sum \left[\tilde{a}_{i} p_{i}^{\mu} + kN \ln\left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_{i}^{0}}{c^{2}}\right) \exp\left(-k \phi^{2} T_{\mu} p_{i}^{\mu}\right)\right]\right\} = k^{2} \phi^{2} \sum \left(\delta \tilde{a}_{i}\right) p_{i}^{\mu} \quad (2.17)$$

This invariant equation, expresses the second law of thermodynamics for reversible processes. The relativistic partition function or sum over states Z is

$$Z = \left\{ \sum \left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_i^0}{c^2} \right) \exp\left(-k \, \phi^2 \, T_\mu p_i^\mu\right) \right\}^N \tag{2.18}$$

and the thermodynamic ψ function is

$$\psi = k \ln Z \tag{2.19}$$

43

A. GEORGIOU

In the form given by (2.19), the function ψ may be used by any inertial observer to obtain the values of the thermodynamic quantities of the system. Thus if T and T_4 are the spatial and temporal components of T_{μ} in σ , we find

$$\boldsymbol{p} = \frac{1}{c^2} T_{\mu} T^{\mu} \frac{\partial \psi}{\partial \boldsymbol{T}}$$
(2.20)

$$\frac{E}{c} = \frac{1}{c^2} T_{\mu} T^{\mu} \frac{\partial \psi}{\partial T_4}$$
(2.21)

with similar expressions in σ^0 . Furthermore, since the eigenvalues of p_i^0 are proportional to $(V^0)^{-1/3}$, it follows that the pressure is given by

$$p^0 = T^0 \frac{\partial \psi}{\partial V^0}$$

3. Phase-Space Formalism

It is possible to formulate relativistic statistical thermodynamics using separate 6N dimensional phase-spaces (Γ -spaces), one for each inertial observer. Liouville's theorem holds for each such Γ space. The element of volume $d\Omega_i$ in the phase-space of the *i*th particle in σ is

and we find that $d\Omega_i = dp_{ix} dp_{iy} dp_{iz} dx_i dy_i dz_i$ $d\Omega_i = (1 - \mathbf{v} \cdot \mathbf{u}_i^0/c^2) d\Omega_i^0$

If we consider a macrocanonical ensemble of systems, each system having N atoms, the distribution functions in σ^0 and σ are

$$Z^{0} = \left\{ \frac{e}{Nh^{3}} \int_{\Gamma_{i}^{0}} \exp(-\theta_{\mu}^{0} p_{i}^{0\mu}) d\Omega_{i}^{0} \right\}^{N}, \qquad Z = \left\{ \frac{e}{Nh^{3}} \int_{\Gamma_{i}} \exp(-\theta_{\mu} p_{i}^{\mu}) d\Omega_{i} \right\}^{N}$$
(3.1)

where h is Planck's constant. It follows that

$$Z = \left\{ \frac{e}{Nh^3} \int\limits_{\Gamma_i^0} \left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_i^0}{c^2} \right) \exp\left(-\theta_\mu p_i^\mu\right) d\Omega_i^0 \right\}^N = Z^0$$
(3.2)

and by setting up spherical polar coordinates in the momentum 3-space of σ^0 , the expression for Z is simplified to

$$Z = \left\{ \frac{4\pi e V^{0}}{Nh^{3}} \int_{0}^{\infty} \left(1 - \frac{\mathbf{v} \cdot \mathbf{u}_{i}^{0}}{c^{2}} \right) \exp\left(-\theta_{\mu} p_{i}^{\mu}\right) p_{i}^{02} dp_{i}^{0} \right\}^{N}$$
(3.3)

A RELATIVISTIC FORM OF STATISTICAL THERMODYNAMICS

Forming the function $\psi = k \ln Z = \psi^0$, the discussion of relativistic macrocanonical ensembles, follows from that of the non-relativistic theory. [See for example, ter Haar (1954).]

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[Note added in proof: After an earlier draft of the present paper was submitted for publication there appeared a paper by Møller on a similar topic [Møller, C. (1968). Mathematisk-fysiske Meddelelser, 36, No. 16]. The treatment is purely classical, though it can be adapted to deal with a quantum mechanical system, provided the energy levels lie together sufficiently densely.]

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