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A relation between the absolute temperature and the arbitrariness in the labelling of the microscopic states of a thermodynamic system

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Fisica teorica. — *A relation between the absolute temperature and the arbitrariness in the labelling of the microscopic states of a thermodynamic system.* Nota di FRANCESCO PEGORARO, presentata (*) dal Corrisp. L. RADICATI DI BROZOLO.

RIASSUNTO. — Si considera un gruppo di trasformazioni che, agendo sulle grandezze che identificano gli stati microscopici di un sistema termodinamico, ne lasciano immutati i numeri di occupazione. Le restrizioni sulla scelta di un principio variazionale da cui derivare le condizioni di equilibrio che si ottengono imponendone la covarianza, individuano, se unite ad alcune generali considerazioni termodinamiche, univocamente il principio.

INTRODUCTION

It is well known that the necessary and sufficient condition for the thermodynamic equilibrium of a given set of systems can be related to the constrained minima or maxima of a suitable thermodynamic potential [see for example [1], p. 81 and foll.].

The extremal points of this potential correspond to the equality of a set of thermodynamic variables of the systems in equilibrium.

This characterization of the equilibrium is valid also for systems which can exchange other quantities besides energy, such as linear momentum, angular momentum etc. i.e. for systems whose states must be labelled by a set of conserved quantities larger than the energy alone.

For each conserved quantity we can define a thermodynamic variable which characterizes the equilibrium (the temperature, the pressure, the average velocity, etc.).

The correspondence between the conserved quantity and the equilibrium variable (energy ↔ temperature, volume ↔ pressure, momentum ↔ average velocity...) can be derived with simple thermodynamic arguments from the transformation properties of the conserved quantity. Namely we want to show that from the knowledge of those transformations (acting on the conserved quantities which label the states of the thermodynamic system) which leave the occupation numbers invariant, we can derive, using only the independent probabilities theorem, a unique variational principle (up to an equivalence) which characterizes the equilibrium.

The relation between the conserved quantity and the equilibrium variable follows simply from the requirement of invariance of the equilibrium condition under those transformations.

Temperature, in particular, has a very simple group theoretical meaning.

(*) Nella seduta del 28 maggio 1974.

In section one we restrict ourselves to purely energetic thermodynamics (i.e. to systems whose states can be completely labelled by the energy values) and we study the energy transformations G which leave the occupation numbers unchanged.

In section two the independent thermodynamic G-invariant functions are constructed, in section three it is proved that only one G-invariant variational principle can be written (the extremality of the total entropy).

Thus the equilibrium variables are uniquely fixed.

In section four more general systems are examined with special regard to the thermodynamics of momentum exchanging systems.

In section five a relativistic theory is briefly discussed.

1. THE GIBBS ENSEMBLE: INVARIANCE PROPERTIES OF THE EQUATIONS RELATING THE PARTITION FUNCTION TO THE THERMODYNAMIC QUANTITIES

Let us consider a Gibbs ensemble of N identical macroscopic systems [1, 2] whose states are labelled by the eigenvalues ε_k of the energy (for the moment we assume that the energy is the only constant of the motion the probability distribution depends on).

As is well known it is possible to define a partition function $Z(\varepsilon_k, \mu)$ such that the equilibrium occupation number a_k of the k^{th} state is

$$a_k = -\frac{N}{\mu}\frac{\partial}{\partial \varepsilon_k}\ln Z \quad ; \quad Z = \Sigma_k\, e^{-\mu\varepsilon_k} \tag{1.1}$$

where μ is a parameter proportional to the inverse of the absolute temperature since it is the integrating factor of the heat supply δQ.

From eq. (1.1) it follows that the mean energy U is

$$U = -\frac{\partial}{\partial\mu}\ln Z\,. \tag{1.2}$$

The labelling of the states by the values of the energy is affected by an indetermination on the choice of the zero values [3] and of the scale of the energy.

Let G be the group (1) acting on the energy values ε through the law

$$(a, b) \in G \qquad (a, b)\cdot\varepsilon = e^{a}(\varepsilon + b)\,. \tag{1.3}$$

The subgroup $(a, 0)$ changes the energy unit, the subgroup $(0, b)$ translates the zero level.

Eq. (1.1) is G-invariant if we define

$$(a, b)\,Z \equiv Z\left(e^{a}(\varepsilon_k + b), e^{-a}\mu\right) = e^{-\mu b} Z \quad ; \quad (a, b)\,\mu = e^{-a}\mu. \tag{1.4}$$

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(1) Mathematically G is the two dimensional Lie group of the automorphisms of **R** into **R**.

From equations (1.2) and (1.4) the correct G-transformation law of U follows:

$$(a\,,b)\,\mathrm{U} = e^{a}\,(\mathrm{U} + b)\,. \tag{1.5}$$

According to the first equation (1.4) Z does not depend on the energy scale and it is transformed like an irreducible, non unitary representation of the energy translations.

This representation is labelled by the parameter μ i.e. by the absolute temperature which can thus be interpreted as the quantity relating the indetermination on the zero level of the energy to the multiplicative indetermination on Z.

According to the second equation (1.4) the absolute temperature is transformed by the changes of unit like an energy.

From the well-known relation between the entropy S and Z

$$\mathrm{S} = \ln \mathrm{Z} - \mu \frac{\partial}{\partial \mu} \ln \mathrm{Z} \tag{1.6}$$

(we have set the Boltzmann constant equal to one) it follows that the entropy is G-invariant.

2. G-INVARIANT FUNCTIONS OF Z

From a brief investigation it follows that the G-invariant functions of Z can be written as functions of

i) the occupation numbers a_k (see eq. (1.1)) and their derivatives with respect to $\mu \frac{\partial}{\partial \mu}$ and $\frac{1}{\mu}\frac{\partial}{\partial \varepsilon_k}$.

The average thermodynamic quantities we can construct in this way are $\mu p \mathrm{V}$ (2) and its derivatives (p is the pressure and V the specific volume)

ii) the entropy $\ln \mathrm{Z} - \mu \frac{\partial}{\partial \mu} \ln \mathrm{Z}$ and its derivatives with respect to $\mu \frac{\partial}{\partial \mu}$. In particular

$$\mu \frac{\partial}{\partial \mu} \mathrm{S} = - \mu^2 \frac{\partial}{\partial \mu^2} \ln \mathrm{Z} \tag{2.1}$$

is the specific heat.

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(2) The volume V is a translation-invariant function of the energy levels ε_k and of μ. From the well-known thermodynamic relation

$$p = - \frac{\partial \mathrm{F}}{\partial \mathrm{V}} \bigg|_{\mu = \mathrm{const}}$$

where F is the free energy we have $\mu p \mathrm{V} = \mathrm{V} \sum_k \frac{\partial \varepsilon_k}{\partial \mathrm{V}} \frac{\partial \ln \mathrm{Z}}{\partial \varepsilon_k} \bigg|_{\mu}$.

3. THE G-INVARIANT VARIATIONAL PRINCIPLE

Let us consider several different Gibbs ensembles which can exchange energy in the form of heat and mechanical work. We generalize the action of the group G through the law

$$(a\,,\,b_{(i)})\,\varepsilon_{(i)} = e^{a}\,(\varepsilon_{(i)} + b_{(i)}) \tag{3.1}$$

where i labels the ensembles and $\varepsilon_{(i)}$ is a generic energy level of the i^{th} system.

The energy unit is the same for all ensembles since the equation $\sum_i \mathrm{d}U_i = 0$ must retain its meaning, while the zero levels can be chosen arbitrarily for each ensemble.

The G-invariant variational principle must depend on a G-invariant function of the conserved quantities i.e. on one of the invariant quantities of section two.

It must be additive i.e. if two or more of the ensembles are in thermal equilibrium then it must be possible to write the same function for a new set of ensembles where those in equilibrium are collected together to form a unique ensemble (this follows from probability theory and independentness assumption).

Finally it must be a monotone function of the conserved quantities independently of the nature of the ensembles. Thus the function f can depend only on the *total entropy* and the only choice for the variational principle is

$$\delta f\,(\mu_i\,,\,\varepsilon_{(i)k}) = \sum_i \frac{\partial f}{\partial \mu_i}\,\delta\mu_i + \sum_i \frac{\partial f}{\partial V_i}\,\delta V_i = 0 \tag{3.2}$$

where f is an arbitrary function of the total entropy of the ensembles. The variation is taken with respect to μ_i and to the thermodynamic variables V_i which are functions of the energy values $\varepsilon_{(i)k}$.

Eq. (3.2) must be supplemented by the conservation conditions (which are G-covariant)

$$\sum_i \delta U_i = 0 \quad ; \quad \sum_i \delta V_i = 0\,. \tag{3.3}$$

Using well known formulae [1] we get

$$\begin{aligned}\sum_i \left(\frac{\partial f}{\partial \mu_i}\bigg|_{\delta U = \delta V = 0} \delta\mu_i + \frac{\partial f}{\partial V_i}\bigg|_{\delta U = \delta V = 0} \delta V_i \right) = \\ = \frac{\mathrm{d}f}{\mathrm{d}s}\left(\sum_i \mu_i \frac{\partial U_i}{\partial \mu_i}\,\delta\mu_i + \sum_i \mu_i \left[\frac{\partial U_i}{\partial V_i} + p_i \right] \delta V_i \right) + \\ + \chi \left(\sum_i \frac{\partial U_i}{\partial \mu_i}\,\delta\mu_i + \sum_i \frac{\partial U_i}{\partial V_i}\,\delta V_i \right) + \rho \sum_i \delta V_i\end{aligned} \tag{3.4}$$

where χ and ρ are Lagrange multipliers and S is the total entropy. Thus

$$\forall f(\mathrm{S}) \;,\; \mathrm{d}f(\mathrm{S}) = 0 \Longleftrightarrow \forall i\,,j \quad \mu_i = \mu_j \qquad \text{and} \quad p_i = p_j\,. \tag{3.5}$$

The equilibrium condition can be thus written in the following way.

i) all the Z_i belong to equivalent representations of the energy translations

ii) their translation invariant derivatives $\partial \ln \mathrm{Z}_i / \partial \mathrm{V}_i$ must be the same so that the equilibrium conditions are explicitly G-covariant.

4. OTHER INTEGRALS OF MOTION. SYSTEMS EXCHANGING LINEAR MOMENTUM

Let us consider a Gibbs ensemble of systems whose states are labelled by the energy ε and by the supplementary integrals of motion $q_1, \cdots, q_n$.

Introducing a Lagrange multiplier for each conserved quantity the occupation numbers are given by

$$a_{i\{j\}} = \frac{e^{-\mu\varepsilon_i - \sum\limits_{\alpha} \lambda_\alpha q_{\alpha\{j\}}}}{\sum\limits_{i\{j\}} e^{-\mu\varepsilon_i - \sum\limits_{\alpha} \lambda_\alpha q_{\alpha\{j\}}}} = \frac{e^{-\mu\varepsilon_i - \sum\limits_{\alpha} \lambda_\alpha q_{\alpha\{j\}}}}{\mathrm{Z}} \tag{4.1}$$

where $\alpha = 1\,, n$ and $i\{j\}$ are the labels of the states.

Eq. (4.1) can be written as (see eq. (1.1))

$$a_{i\{j\}} = -\frac{\mathrm{N}}{\mu}\,\frac{\partial \ln \mathrm{Z}}{\partial \varepsilon_i}\left(\Pi_\beta \frac{1}{\lambda_\beta}\,\frac{\partial \ln \mathrm{Z}_\beta}{\partial q_{\beta\{j\}}}\right) \tag{4.2}$$

where

$$\mathrm{Z}_\beta = \Sigma_{j_\beta, j_n}\, e^{-\sum\limits_{\beta}^{n}{}_{\alpha} \lambda_\alpha q_{\alpha\{j\}}}\,.$$

In general the Hamiltonian will depend upon the q's. It may be more transparent to separate the energy values ε_i into an intrisic part η_i (independent of the q's) and a function of the q's. Obviously the transformation of the q's which do not change the values of the occupation numbers depend upon the form of these functions.

Let us consider an ensemble of systems whose states are labelled by the energy and the linear momentum and with a Hamiltonian which can be split into an intrinsic and a kinetic part i.e.

$$\varepsilon = \eta + \frac{|\vec{p}\,|^2}{2m} \tag{4.3}$$

where m is the mass of the system.

We can thus rewrite eq. (4.1) in the form

$$(4.4) \qquad a_{ij} = \frac{e^{-\mu\eta_i - \frac{\mu}{2m}|\vec{p}|_j^2 + \vec{\lambda}\cdot\vec{p}_j}}{\sum_{ij} e^{-\mu\eta_i - \frac{\mu}{2m}|\vec{p}|_j^2 + \vec{\lambda}\cdot\vec{p}_j}} = \frac{e^{-\mu\eta_i - \frac{\mu}{2m}\left(\vec{p}_j - \frac{m\vec{\lambda}}{\mu}\right)^2 + \frac{|\vec{\lambda}|^2 m}{2\mu}}}{Z(\mu, \lambda, \eta, \vec{p})} .$$

The mean energy is given by

$$(4.5) \qquad U = -\frac{\partial \ln Z}{\partial \mu}$$

the mean momentum by

$$(4.6) \qquad \vec{P} = \frac{\partial \ln Z}{\partial \vec{\lambda}} = \frac{m\vec{\lambda}}{\mu} = m\vec{v}$$

i.e. the Lagrange multiplier $\vec{\lambda}$ can be interpreted as the mean velocity $\vec{v}$ multiplied by the absolute temperature.

Thus the intrinsic mean energy is

$$(4.7) \qquad U_{\text{intr}} = -\frac{\partial \ln Z}{\partial \mu} - \frac{\vec{\lambda}}{2\mu} \cdot \frac{\partial \ln Z}{\partial \vec{\lambda}} .$$

Eq. (4.4) is covariant under the action of the group G, defined in section one, if

$$(4.8) \qquad \vec{p}_j \to e^a \vec{p}_j \qquad m \to e^a m \qquad \text{and} \quad \vec{\lambda} \to e^{-a} \vec{\lambda} \qquad (\Rightarrow \vec{P} \to e^a \vec{P}) .$$

The only transformations on $\vec{p}_j$ we can add to those of G without changing the occupation numbers are the Galileo transformations

$$(4.9) \qquad \vec{p}_j \to \vec{p}_j + m\vec{w} \qquad \vec{\lambda} \to \vec{\lambda} + \frac{\vec{w}}{\mu} \qquad \eta_j \to \eta_j$$

$$\left(\Rightarrow U \to U + \frac{m|\vec{w}|^2}{2} + \frac{m\vec{\lambda}}{\mu} \cdot \vec{w} , \ \vec{P} \to \vec{P} + m\vec{w}\right) .$$

We call G′ the semidirect product of energy and the Galileo transformations.

It is easily seen that the "entropy"

$$(4.10) \qquad S = \ln Z - \mu \frac{\partial \ln Z}{\partial \mu} - \vec{\lambda} \cdot \frac{\partial \ln Z}{\partial \vec{\lambda}}$$

is G′-invariant.

Since from equation (4.6) it follows

$$(4.11) \qquad Z = e^{\frac{m}{2}\frac{|\vec{\lambda}|^2}{\mu}} \mathbf{Z}(\mu, \varepsilon_i)$$

then

$$S = \frac{m}{2}\,\frac{|\vec{\lambda}|^2}{\mu} + \ln \mathbf{Z}(\mu\,,\,\varepsilon_i) + \mu U - \frac{m|\vec{\lambda}|^2}{\mu} = \ln \mathbf{Z}(\mu\,,\,\varepsilon_i) + \mu U_{\text{intr}} \tag{4.12}$$

i.e. S is the correct entropy.

Let us consider a set of ensembles (just as in sec. 3); the generalization of the group G′ is obtained by letting the zero energy levels vary independently while, on the contrary, the Galileo transformations must obviously be the same for all the ensembles. Following the same argument we used in section three, we find that the equilibrium variational principle must be written in terms of a function of the total entropy.

The conservation equations are

$$\sum_i dU_i = 0 \qquad \sum_i dV_i = 0 \qquad \sum_i d\vec{P}_i = 0\,. \tag{4.13}$$

Let f be a function of the total entropy S, then (summation is assumed over dummy spatial indices $\alpha\,,\beta = 1\,,2\,,3$)

$$\begin{aligned}\sum_i \left(\frac{\partial f}{\partial \mu_i}\bigg|_{\delta U=\delta V=\delta\vec{P}=0} \delta\mu_i + \frac{\partial f}{\partial V_i}\bigg|_{\delta U=\delta V=\delta\vec{P}=0} \delta V_i + \frac{\partial f}{\partial \lambda_{\alpha i}}\bigg|_{\delta U=\delta V=\delta\vec{P}=0} \delta\lambda_{\alpha i}\right) = \\ = \frac{df}{ds}\sum_i\left(\mu_i \frac{\partial U_i}{\partial \mu_i}\,\delta\mu_i - \lambda_{\alpha i}\frac{\partial P_{\alpha i}}{\partial \mu_i}\,\delta\mu_i + \mu_i\frac{\partial U_i}{\partial \lambda_{\alpha i}}\,\delta\lambda_{\alpha i} + \right. \\ \left. - \lambda_{\alpha i}\frac{\partial}{\partial\lambda_{\beta i}}(P_{\alpha i})\,\delta\lambda_{\beta i} + \mu_i\left[\frac{\partial U_i}{\partial V_i} + p_i\right]\delta V_i\right) + \\ + \rho\left(\sum_i \frac{\partial U_i}{\partial \mu_i}\,\delta\mu_i + \sum_i \frac{\partial U_i}{\partial\lambda_{\alpha i}}\,\delta\lambda_{\alpha i}\right) + \\ + \chi_\alpha\left(\sum_i \frac{\partial P_{\alpha i}}{\partial \mu_i}\,\delta\mu_i + \sum_i \frac{\partial P_{\alpha i}}{\partial \lambda_{\beta i}}\,\delta\lambda_{\beta i}\right) + \tau\sum_i \delta V_i = 0\end{aligned} \tag{4.14}$$

($\rho\,,\vec{\chi}$ and τ are Lagrange multipliers) implies

$$\forall_{i,j} \qquad \begin{aligned} \mu_i &= \mu_j \\ p_i &= p_j \\ \vec{\lambda}_i &= \vec{\lambda}_j \end{aligned}$$

i.e. two ensembles are in equilibrium if they have the same temperature, pressure and mean velocity.

These results were a priori obvious. It may be however interesting to see how all these conditions can be derived from a unique G-invariant variational principle (e.g. exactly the same procedure applied to charged systems, whose energy is a quadratic homogeneous function of the total charge, would imply that two systems are in equilibrium if they have the same potential).

5. RELATIVISTIC EQUILIBRIUM

The formulae of the previous section are more transparent if we consider a covariant Gibbs ensemble: a zero or a first order expansion in the average velocity gives the results of section three or four respectively.

The occupation numbers of a relativistic ensemble [1] are

$$a_k = -\frac{N\mu^\alpha}{\mu^2}\frac{\partial \ln Z}{\partial p_k^\alpha} \tag{5.1}$$

where Z is the relativistic partition function

$$Z = \sum_i e^{-\mu_\alpha p_i^\alpha} \tag{5.2}$$

p_i^α is the four momentum of the i^{th} state and μ_α is a Lagrange multiplier which behaves as a time-like four vector. Thus it follows

$$P^\alpha = -\frac{\partial \ln Z}{\partial \mu_\alpha} = \frac{M}{|\mu|}\mu^\alpha \tag{5.3}$$

where P^α is the mean four momentum, M is its length and $|\mu| = \sqrt{\mu^2}$ is the length of the four vector μ^α. The physical interpretation of μ^α follows easily: μ^α is the inverse absolute temperature four vector, namely $|\mu|$ is the inverse of the absolute (scalar) temperature while $\mu^\alpha/|\mu|$ is the mean four velocity of the ensemble. Eq. (5.1) is invariant under the Lorentz group and the group G whose transformations are now

$$p_i^\alpha \rightarrow p_i^\alpha + \pi_i^\alpha \tag{5.4}$$

where π_i^α is an arbitrary four vector and

$$M \rightarrow e^a M \quad ; \quad |\mu| \rightarrow e^{-a}|\mu| . \tag{5.5}$$

When considering a set of ensembles the action of G can be generalized by considering independent momentum translations on each ensemble.

Following the usual argument we prove that the variational principle must involve a function of

$$S = \sum_i \ln Z_i - \mu_i^\alpha \frac{\partial \ln Z_i}{\partial \mu_i^\alpha} \tag{5.6}$$

(sec. eq. 4.10) where i labels the ensembles.

The equilibrium conditions are

$\forall_{i,j}\ \mu_i^\alpha = \mu_j^\alpha$ i.e. same temperature and mean velocity

$p_i = p_j$ i.e. same pressure in the rest frame.

Thus we can say that two relativistic ensembles are in equilibrium iff:

i) the partition functions belong to equivalent representations of the four momentum translations;

ii) their invariant derivatives $\partial \ln Z_i/\partial V_i$ are the same ($\partial \ln Z_i/\partial V_i$ is computed in the rest frame).

It must be emphasized that the momentum translations do not correspond to a microscopic or macroscopic invariance of the system. It is easy to see that the second part of eq. (5.3) is not valid (since the rest frame of the system is changed and therefore the classic limit is perturbed) and that we can get negative " masses ".

The G-invariance expresses only the homogeneity of the summation procedure in phase space used to compute the partition function i.e., as we pointed out in sec. 1, the ambiguity in the labelling of the microscopic states.

If the partition function is assumed as the starting point for the construction of all the thermodynamic quantities, then obviously the equilibrium conditions must be expressed through the G-invariant quantities we can derive from it.

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