THE CONCEPT OF SYSTEM AND THE PHYSICAL SIGNIFICANCE OF THE QUANTITIES WORK AND HEAT

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RESUMO

Neste artigo o conceito de sistema é relacionado com os conceitos de entropia, trabalho e calor. Através da análise de três modelos mostra-se que a arbitrariedade na escolha do sistema é função da existência de partes do Universo cuja energia é apenas função das variáveis de deformação. Por esta razão estas parcelas da energia podem ou não ser incluídas na energia interna ou no termo trabalho. Tendo isto presente propõe-se uma nova interpretação da quantidade calor e um enunciado não ortodoxo do Segundo Princípio da Termodinâmica.

ABSTRACT

In this paper the concept of system is related to the concepts of entropy, work and heat. Through the analysis of three models it is shown that the arbitrariness in the choice of the system is related to the existence of parts of the Universe whose energy is only a function of the deformations variables.

For this reason those parts may or may not be included in the system or in the work term. With this in mind we propose a new interpretation of the quantity heat and a non ortodox enunciation of the Second Principle of Thermodynamics.

I INTRODUCTION

The conceptual difficulties of thermodynamics have lately been the object of special attention in the literature [1].

With this work we intend to show that it is possible to understand the origin of some contradictions still existing in thermodynamics [2] through the analysis of three models which make easy the understanding of the physical significance of the concepts involved, as well as the relation of the arbitrariness in the system definition and the concepts of work an heat [3].

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II THE SYSTEM AND ENTROPY

We shall start by assigning the number 1, 2 and 3 to the models to be considered.

Model 1 is a gas contained in a vessel provided with a piston, the effect of the gravitational field upon the gas being negligible.

Model 2 is identical to 1, except that the effect of gravity upon the gas is not negligible.

Model 3 consists of an ensemble of magnetic moments without interaction in the presence of a magnetic field.

For each model 1, 2 and 3 two situations, described as *a* and *b*, will be considered.

1*a* indicates that the piston is outside the system. The System is only the gas (we consider the ideal situation where the walls can only intervene energetically in the process through the vertical movement, parallel to the field, of the piston). In this case the internal energy is only the kinetic energy due to the movement of the gas atoms.

$$U_{1a} = \sum_i \mathrm{ukin}_i \tag{1}$$

where ukin_i is the kinetic energy of particle i.

1*b* indicates that the piston belongs to the system. In this case the internal energy is

$$U_{1b} = \sum_i \mathrm{ukin}_i + \phi_e \tag{2}$$

where ϕ_e is the potential energy of the piston due to the gravitational field.

In 2*a* the potential energy of the gas is considered to be outside the internal energy, 2*a* corresponding to 1*a*.

2b includes the potential energy of the gas in the internal energy, thus corresponding to 1b.

$$U_{2a} = \sum_i \text{unkin}_i, \quad (3)$$

$$U_{2b} = \sum_i \text{unkin}_i + \phi_g, \quad (4)$$

where ϕ_g is the potential energy of the gas owing to the fact that the gas atoms are on a gravitational field g.

Similarly, we have

$$U_{3a} = \sum_i \text{uspin}_i \quad (5)$$

$$U_{3b} = \sum_i \text{uspin}_i + \epsilon \quad (6)$$

where uspin_i is the energy of the magnetic moment i on the field and ϵ is the energy of the magnetic field.

The energy of a system is a function of the entropy S and of the deformation variables x_k,

$$U = U(S, x_k). \quad (7)$$

We thus have

$$dU = (\partial U/\partial S)\, dS + (\partial U/\partial x_k)\, dx_k \quad (8)$$

where *d* is the exterior derivative operator.

For a dP elementary variation in space (S, x_k), whatever the direction of dP is (not necessarily tangent to the surface of the reversible transformations — S = const.) we have

$$dU = \langle dU, dP\rangle \quad (9)$$

($\langle dU, dP\rangle$ is the contraction of *d*U form with the dP vector).

The dU elementary variation due to dP is, therefore,

$$dU = (\partial U/\partial S)\, dS + (\partial U/\partial x_k)\, dx_k \quad (10)$$

This relation is valid along a quasi-static transformation which should not be taken as reversible, since reversibility is verified for a particular dP (dS = 0).

Since

$$\left(\frac{\partial U}{\partial S}\right)_{x_k} = T \quad (11)$$

and

$$(\partial U/\partial x_k)_S = X_k, \quad (12)$$

we have

$$dU = TdS + X_k\, dx_k. \quad (13)$$

Relation (13) is valid for a quasi-static transformation which needs not be a reversible one.

For model 1a we have

$$U_{1a} = U_{1a}(S_{1a}, V) \quad (14)$$

where V is the gas volume,

$$dU_{1a} = TdS_{1a} - P_{1a}\, dV \quad (15)$$

and $P_{1a} = -\partial U_{1a}/\partial V$.

In 1b we have

$$U_{1b} = U_{1a} + m_e\, gh \quad (16)$$

where m_e is the piston mass and h the piston heigh relative to the bottom of the vessel which contains the gas.

If A stands for the (constant) section area of the vessel, $V = h \times A$, we have:

$$U_{1b} = U_{1a} + m_e g\; V/A. \quad (17)$$

Given $U_{1b} = U_{1b}(S_{1b}, V)$ we have:

$$dU_{1b} = TdS_{1b} + \partial U_{1b}/\partial V\, dV \quad (18)$$

and from (17), (15) and $S_{1b} = S_{1a}$ (the piston does not contribute to the entropy) we get:

$$dU_{1b} - m_e g/A\, dV = TdS_{1a} - P_{1a}\, dV = dU_{1a} \quad (19)$$

If the transformation is reversible it is worth noting that

$$dU_{1b} = -P_{ext}\, dV, \quad (20)$$

where P_{ext} is the external pressure and $P_{ext} = P_{1a} - m_e g/A$.

It should be pointed out that, since $S_{1b} = S_{1a}$ and $\phi_e = \phi_e(V)$, (15) can be obtained from (18).

We shall now consider 2. If $U_{2a} = U_{2a}(S_{2a}, x_k)$ then

$$dU_{2a} = \partial U_{2a}/\partial S_{2a}\, dS_{2a} + \partial U_{2a}/\partial x_k\, dx_k. \quad (21)$$

If $U_{2b} = U_{2b}(S_{2b}, x_k)$ and $S_{2b} = S_{2a}$, it was then easy obtain dU_{2a} from dU_{2b} in the same way as we have obtained (15) from (18).

However, if $S_{2b} = S_{2a}$, this is not generally possible. This is what we are going to verify by the microscopic analysis of model 2.

Model 3 is analogous to 1, there being, therefore, arbitrariness in the inclusion of the field energy in the system (inclusion of the piston in 1b),

$$dU_{3a} = TdS_{3a} + \partial U_{3a}/\partial x_k\, dx_k, \quad (22)$$

$$dU_{3b} = TdS_{3b} + \partial U_{3b}/\partial y_k\, dy_k. \quad (23)$$

Since $U_{3b} = U_{3a} + \epsilon$, we have

$$dU_{3a} = TdS_{3b} + \partial U_{3b}/\partial y_k\, dy_k - d\epsilon.$$

If $S_{3b} = S_{3a}$, then

$$dU_{3b}/\partial y_k\, dy_k - d\epsilon = \partial U_{3a}/\partial x_k\, dx_k.$$

It is possible to show [4] the following relations

$$dU_{3a} = TdS - pdV - \overline{M}dH$$

$$dE^* = TdS - pdV - Hd\overline{M}$$

with $E^* = U_{3a} + \overline{M}H = U_{3b} - VH^2/8\pi$ and $S = S_{3a} = S_{3b}$.

Microscopic Analysis of 2

Let us consider the phase space x, y, z, p_x, p_y, p_z. The entropy is givin by $S = K \Sigma \overline{N}_i \ (1 - \ln \ \overline{N}_i)$ where $\overline{N}_i = e^{-(\alpha + \beta u_i)}$ [5], $u_i = \frac{1}{2} m \ v_i^2 + \phi_i$ and ϕ_i is the potential energy of the mass m due to gravity (m stands for the mass of a gas particle).

The normalization conditions which make it possible to determine α and β are:

$$U = \sum_i u_i \ \overline{N}_i, \tag{24}$$

$$N = \sum_i N_i. \tag{25}$$

We can then see that U contains a term due to the potential energy.

Replacing $\overline{N}_i$ in $S = K \ \Sigma \ \overline{N}_i (1 - \ln \ \overline{N}_i)$ one obtains

$$S = K [N + N \ \ln \ V_e/N + + 3/2 \ N \ \ln (2\pi m/\beta h^2) + \beta U] \tag{26}$$

where $V_e = \int_{x,\,y,\,z} e^{-\beta\phi} \ dx \ dy \ dz$.

It is therefore clear that both U and S contain terms due to the potential energy, which shows that the gas in the gravitational field is described by *2b* not by *2a*. In fact it is not possible to consider $U = U_{2a} = U_{2a}(S_{2a}, V)$ with $S_{2a} = S_{2b}$ because the potential energy contributes here to the entropy and for the energy in the way expressed by (26). The energy of the system here is necessarily U_{2b} and we can not put out the potential energy like in the model 1 because (26) does not permit that partition.

III INTERNAL ENERGY AND ENTROPY — THE SECOND PRINCIPLE

In order to be characterized, the energy of a system must have the entropy variable. In fact [6], if a system goes back to the initial deformation variables [7] the energy is higher than, or equal to the initial energy (equality is verified in the reversible transformation).

It is nevertheless obvious that, once the SYSTEM is defined as the part of the "Universe" that contains the entropy variables, we can add to it other parts that do not depend on the entropy and have a "new" SYSTEM with the same entropy (it is the case of models 1 and 3).

In model 2 is obvious that the potential energy of the gas is not analogous to the potential energy of the piston.

In model 1 and 3 we have arbitrariness in the choice of the system because the piston or the field don't contribute to the entropy and because of that we can put the energy of the piston or the energy of the magnetic field associated to the work. This is not the case with the potential energy and model 2.

The quantity heat is sometimes associated with the kinetic energy of the gas molecules or, and this is the dominant orthodox position, it is defined on the basis of the First Principle. It is then stated that heat is what complements work in order to obtain the variation of internal energy.

If we are careful to attribute a physical sense to the quantity work [10] by associating it with those kinds of energy that have a character of reversibility (like the piston and the magnetic field) and which, according to Gibbs [11] [9], may be associated with the rise or fall of a weight, we can enunciate in a more general sense that heat (internal energy) cannot be transformed into work if the deformation variables are the same (i.e., if they go back to their initial value). In model 2 the internal energy (heat) contains a term of potential energy which contributes to the variation of entropy. Once the system goes back to its initial configuration, the work turns into heat — degradation of energy [12]. *Thus, once the variation of entropy has been chosen in the sense of variation of heat ($\partial U/\partial S > 0$) it is possible to state that the entropy of a SYSTEM increases or remains constant.* We have therefore shown how easy it is possible to pass from the language of heat to the one of entropy in the enunciation of the Second Principle. We affirm in conclusion that the concepts of work and heat must be associated through the "Second Principle of Thermodynamics" when stating the impossibility of the internal energy (heat) being converted into work (kind of energy that are reversible because is not function of the entropy) in a transformation where the deformation variables are the same at the begining and at the end of the transformation.

This non-symmetry implies the existence of the quantity entropy whose variation is larger than, or equal to, zero ($\frac{\partial U}{\partial S} > 0$ has been arbitrated). It is therefore essencial to use the designation heat and work in the precise sense sugested here and not in the sense resulting from $dU = dW + dQ$ [13].

We finally reafirm that, energy being a function of entropy and of the deformation variables, it is not generally possible to divide the system into sub-systems, assuming only the additivity of the energy. The entropy of the system must allow this partition.

It is however clear that if the system permits a partition into n sub-systems so that $U = \sum_i U_i$ and $S = \sum_i S_i$, the previous enunciation apllies to the whole (SYSTEM) and not to the part (sub-systems). If $U_i = U_i(S_i, x_i)$, then $dU_i = TdS_i + X_i\, dx_i$ is also obviously verified in a quasi-static transformation.

A deep understanding of the difficulties associated with the concept of heat implies a conceptual revision of the concepts of force and work, which has generally precluded the possibility of attributing a physical significance to the First Principle of Thermodynamics [14] [15].

We believe that out work will, in a new way, contribute to the elucidation of such conceptual difficulties, avoiding those conflicts originating in Clausius formulation that has unfortunately been recovered through the Caratheodory-type formulations. We are refering to the interpretation of Caratheodory formulation through the First Principle, $dU = dW + dQ$, [16] [17].

In the light of what has been said, we believe to be contributing to the use of an adequate language that will allow an easy understanding of some of the formulations [18] whose importance has lately been increased due to the necessity of optimizing energy utilization but whose interpretation is difficult from an orthodox thermodynamics point of view.

In a recent paper [19] Hans Fuchs proposes (following others) the identification between Heat and entropy. Though the motive for this identification was, with simplicity, to introduce the entropy concept considered essential and primordial (this is also our point of view) [6], this can be achieved by identifyint Heat (an energy concept) with internal energy. The difficulty to accept this identification is related to the difficulty in understanding that heat cannot be transformed into work only if the deformation variables are the same after the transformation [6]. The existence of equilibrium and the energy concept are enough for the conceptualization of the Energy-Entropy Principle [6] [20] [21] [22].

REFERENCES

[1] Serrin, J., New Perspectives in Thermodynamics (Springer-Verlag) (1986).
[2] Yuen, C.K., Am. J. Phys. 38(2) (1970).
[3] Pauli, W., Thermodynamics and the Kinetic Theory of Gases, (MIT Press) p. 94 (1973).
[4] Reif, F., Fundamentals of Statistical and Thermal Physics (McGraw-Hill Kogakusha, Ltda.) pp. 438-448 (1965.
[5] Allis, W.P. and Herlin, M.A., Thermodynamics and Statiscal Mechanics, (McGraw-Hill Book Company, Inc.) pp. 168-170 (1952).
[6] Rodrigo de Abreu, Técnica 1 and 2 (1985).
[7] Pau-Chang Lu, Am. J. Phys. 50(3) (1982).
[8] Arzélies, H., Thermodinamique Relativiste et Quantique, (Gauthier-Villars) pp. 681-682.
[9] Pauli, W., Thermodynamics and the Kinetic Theory of Gases, (MIT Press) p. 5 (1973).
[10] Reif, F., Fundamentals of Statistical and Thermal Physics, (McGraw-Hill Kogakusha, Ltd.) p. 115 (1965).
[11] Laufer, G., Am. J. Phys. 51(1) (1983).
[12] Planck, Max, Introduction to Theoretical Physics, Vol. 5 (Mac Millan and Co. Ltd.) p. 51 (1932).
[13] Balescu, R., Physica, 40, 309 (1968).
[14] Rodrigo de Abreu, Thésis, Lisbon (1983).
[15] Curzon, A.E. and Leff, H.S., Am. J. Phys. 47(4) (1979).
[16] Landsberg, P.T., Am. J. Phys. 51(9) (1983).
[17] Sears, F.W., Am. J. Phys., 31(10) (1963).
[18] Ahern, J.E., The exergy method of energy systems analysis, Wiley-Interscience, John Wiley & Sons) pp. 43-44 (1980).
[19] Fuchs, Hans U., Am. J. Phys. 55(3) (1987).
[20] M. de Abreu Faro and Rodrigo de Abreu, A One-Dimensional Model of Irreversibility (to be published).
[21] M. Rebelo da Silva e Rodrigo de Abreu, Termodinâmica — uma visão inovadora (to be published) 1987.
[22] Rodrigo de Abreu, Heat, Internal Energy and Entropy, in the teaching of introductory Thermodynamics (to be published).