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Abstract

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PHYSICS

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ON THE NONADDITIVE ENTROPY OF A THERMALLY INHOMOGENEOUS SYSTEM

(Presented by Academician M. A. Leontovich, 19 XI 1964)

In thermodynamics, so-called thermally inhomogeneous systems are considered. By these one usually means systems in which the temperatures of different parts of the system are different (^{1}). This state is maintained, for example, by means of adiabatic partitions. A formal representation of thermally inhomogeneous systems led P. S. Epstein to the conclusion that the entropy of such systems has a nonadditive character (^{2,3}). If one restricts oneself to the case of a two-temperature system, with the temperature and entropy of one part of the system τ_1 and S_1, respectively, and of the other τ_2, S_2, then it is asserted (^{3}) that the entropy of the whole system is related to the entropies of both parts by the relation:

$$\tau\, dS = \tau_1 dS_1 + \tau_2 dS_2, \tag{1}$$

where τ is the formally defined temperature of the whole system.

It is essential that in the system under consideration the interaction of the two parts is assumed to be negligibly small. Accordingly, in the transition to an ordinary thermally homogeneous system, the condition $\tau_1 = \tau_2 = \tau = T$ holds, where T is the thermodynamic temperature. The derivation of relation (1) is elementary: it is based on a formal extension of the theorem on the existence of an integrating factor for the quantity of heat to the case of thermally inhomogeneous systems (^{3}). As is known, this theorem follows directly from Carathéodory' s principle of the existence of adiabatic inaccessibility (^{1}). Thus, the formal derivation of (1) is essentially based on applying Carathéodory' s principle to thermally inhomogeneous systems.

However, one can construct an example of a concrete thermally inhomogeneous system in which an integrating factor does not exist. This example was constructed by T. A. Ehrenfest-Afanassjewa (^{4}) and is given in (^{1}). The system consists of two moles of ideal gases with different heat capacities c_{v1} and c_{v2}, separated by an adiabatic movable piston that ensures equal pressures at different temperatures. For the Ehrenfest-Afanassjewa system, the principle of the existence of adiabatic inaccessibility is therefore not fulfilled. On the basis of this example it is asserted in (^{4}) that Carathéodory' s principle does not follow from the second law of thermodynamics precisely in the case of thermally inhomogeneous systems. The same idea is expressed by M. A. Leontovich (^{1}). As an objection to the fulfillment of Carathéodory' s principle in the case of thermally inhomogeneous systems, it is further pointed out here that it is impossible in such systems to define an isothermal process. (This definition plays an important role in deriving Carathéodory' s principle from the second law.)

Thus, on the question of applying Carathéodory's principle to thermally inhomogeneous systems, there exist two opposing points of view. With an affirmative solution of the question, according to P. S. Epstein, the entropy of a thermally inhomogeneous system is not additive with respect to the entropies of the parts of the system. From the opposite point of view, expressed

According to T. A. Ehrenfest-Afanassjewa and M. A. Leontovich, the entropy of a system with different temperatures is the sum of the entropies of its parts. The interaction of the parts of the system, as stated above, is negligibly small. Before drawing general conclusions, we shall indicate an example of a thermally inhomogeneous physical system for which an integrating factor exists for the quantity of heat. For this example, consequently, relation (1) is satisfied, and τ and S have specific expressions in terms of the physical parameters of the system. At first glance this example confirms P. S. Epstein' s point of view, but analysis leads to the opposite conclusion.

Consider an electron-ion ideal plasma. The condition of ideality of the plasma, meaning the smallness of the potential energy of the Coulomb interaction of charged particles in comparison with the kinetic energy of their thermal motion, is the inequality (^{5}):

$$D \gg d, \qquad D = (k\theta/4\pi e^2 nZ)^{1/2}, \qquad d = 1/(Zn)^{1/3}. \tag{2}$$

In (2), D is the Debye radius, expressed in terms of the electron temperature of the plasma θ and the density of plasma ions n; d is the mean distance between plasma particles; k is Boltzmann' s constant; e is the elementary charge; Ze is the charge of a plasma ion. In the plasma the condition of electrical neutrality is well satisfied:

$$n_e = Zn. \tag{3}$$

Under the condition of ideality of the plasma (2) and taking (3) into account, the equations of state of a two-temperature plasma with ion temperature $T \neq \theta$ are formulated in the well-known way:

$$p_i = NkT, \qquad p_e = ZNk\theta, \qquad E_i = \tfrac{3}{2}p_i/\rho, \qquad E_e = \tfrac{3}{2}p_e/\rho,$$
$$\rho = NM, \tag{4}$$

where the internal energies of the ion and electron components of the plasma are referred to unit mass of the ion component, with M the mass of an ion.

The consideration of a two-temperature state of a plasma is justified in kinetic theory (^{6}). The times for establishment of an equilibrium Maxwellian distribution within each of the two plasma components separately are considerably smaller than the time for equalization of their temperatures T and θ (approximately $Z\sqrt{M/m}$ times smaller for the ions, for which the relaxation time is the largest). In various nonstationary processes, conditions are often created in which a nonequilibrium two-temperature state of the plasma arises. An important particular example of such processes is a shock front propagating in the plasma. The ideality condition (2), which leads to the equations of state (4), the condition of electrical neutrality (3), and the definition of a quasistationary state with $T \neq \theta$ are all, of course, approximate with respect to a real plasma. Therefore the thermodynamic functions introduced below also have an approximate character. Small corrections to them may be taken into account in the next approximation.

Let us write the thermodynamic relations for both components of the plasma, referring extensive thermodynamic quantities to unit mass of the ion component. Then the volume $V = 1/\rho$ is the specific volume.

$$dE_i = T\,dS_i - p_i\,dV, \tag{5}$$

$$dE_e = \theta\,dS_e - p_e\,dV, \tag{6}$$

where S_i and S_e are the entropies of the ions and electrons of the plasma, respectively.

We shall show that the quantity of heat dQ in this case has an integrating factor, and we shall find it explicitly. Taking (4) into account,

$$dQ = dE + p\,dV = \tfrac{3}{2}R\,d(T + Z\theta) + R(T + Z\theta)\,d\ln V. \tag{7}$$

In (7), $R = kN/\rho = k/M$ is the gas constant. As is easy to verify, the integrating factor of (7) is

$$1/\tau = A/(T + Z\theta), \tag{8}$$

where A is an arbitrary constant quantity. In order that τ coincide with the thermodynamic temperature of the plasma in the case $T = \theta$, we put $A = Z + 1$. Integrating (7), multiplied by τ^{-1}, and introducing the notation

$$dS^* = \delta Q/\tau, \tag{9}$$

$$S^* = R(Z+1)\ln\left[(T + Z\theta)^{3/2} V\right] + S_0^*. \tag{10}$$

The state function S^* may be called the nonadditive "entropy" of the plasma. Indeed, from (5), (6), and (9) it follows that:

$$\frac{T + Z\theta}{1 + Z}\, dS^* = T\, dS_i + \theta\, dS_e. \tag{11}$$

Only in the case of complete equilibrium $T = \theta = T_0$, according to (8) and (10), $\tau = T_0$, and S^* coincides with the entropy of the plasma $S = S_i + S_e$.

Let us make a small digression in order to clarify the properties and physical meaning of the nonadditive "entropy" S^* and of the corresponding "temperature" τ. From (10) it is evident that S^* is the entropy of such a model of plasma in which the electron and ion gases are separated by an adiabatic partition, and states with any value of $T - Z\theta$ at a given τ are equilibrium states. The role of temperature in such a model is played by the quantity τ, which has the meaning of the mean internal energy per elementary particle. As is usually done [5], it is easy to show that $\delta S^* \geq 0$ when heat is transferred from plasma particle 1 to plasma particle 2, if $\tau_1 \geq \tau_2$.* Similarly, $\delta S^* \geq 0$ if the volume contraction occurs in the plasma particle with the lower initial pressure. This proof is in no way connected with the specific form of S^* and τ; only two relations are used,

$$(\partial S^*/\partial E)_V = 1/\tau, \qquad (\partial S^*/\partial V)_E = p/\tau, \tag{12}$$

which S^* from (10) and τ from (8) satisfy. When the characteristic times are much shorter than the time for the establishment of equilibrium between electrons and ions, the introduced functions S^* and τ, consequently, determine the thermodynamic behavior of a two-temperature plasma. It should be noted, however, that the special method of defining τ, which depends on Z, excludes the possibility of describing the establishment of equilibrium between two plasma particles with different Z. In other words, in artificial thermodynamics it is impossible to consider a plasma particle with $Z = Z_0$ in a thermostat of arbitrary physical properties. Only a thermostat consisting of exactly the same plasma with $Z = Z_0$ is possible. Finally, thermodynamics with S^* and τ may fail to reflect the intermediate stages of the process when thermal equilibrium is established between plasma particles 1 and 2. For example, if $\tau_1 > \tau_2$, but $\theta_1 < \theta_2$ and $T_1 > T_2$, S^* will only increase until $\tau_1 = \tau_2$. In fact, it follows from plasma kinetics [6] that the electron temperatures first equalize, i.e., at first heat will pass, on the contrary, 2 → 1. The resulting heat flow will be directed from 1 to 2. Initial conditions of this type may be called nonmonotonic.

Thus, with the aid of the functions S^* and τ, the thermodynamics has been obtained not of a real plasma particle, but of its idealized model with a heat-insulating partition between the electrons and ions, in which any states with a given τ (but with different values of $T - Z\theta$) are equilibrium states, with a thermostat made of plasma with the same ionic charge, and with monotonic initial conditions.

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* The term "plasma particle" is used in the usual hydrodynamic sense.

Now let us return again to the general question of the application of the Carathéodory principle to thermally inhomogeneous systems. Along with the negative example of T. A. Ehrenfest-Afanassjewa, an example was constructed above in which, in the form (11), the nonadditive entropy (1) is determined as applied to a physically important system—an ideal electron-ion plasma. In this same case it is possible to determine the temperature of the system τ as the mean internal energy per one elementary particle. Therefore the argument in (1,4), that the Carathéodory principle does not follow from the second law of thermodynamics precisely in the case of thermally inhomogeneous systems, based on general thermodynamic considerations and the indication of negative examples, is insufficient. The strict untenability of the application of the Carathéodory principle to thermally inhomogeneous systems, carried out in the works of P. S. Epstein (2,3), is revealed only when such an artificial thermodynamics is compared with the basic conclusions of statistical thermodynamics. Indeed, the obtaining of a nonadditive "entropy" as a result of applying the Carathéodory principle to a thermally inhomogeneous system—an ideal plasma —contradicts the additivity of the statistical entropy in the case of statistically independent systems—the electron and ion components of the plasma:

$$S(E) = S_i(E_i) + S_e(E_e), \tag{13}$$

where $E = E_i + E_e$ is the total internal energy of the plasma particle. For any other systems, except thermally inhomogeneous ones, the Carathéodory principle is identical with the second law.

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Note: Figure translations are in progress. See original paper for figures.