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THERMODYNAMICS AND RELATIVITY. II

By PROFESSOR RICHARD C. TOLMAN
CALIFORNIA INSTITUTE OF TECHNOLOGY

(5) CONSEQUENCES OF RELATIVISTIC THERMODYNAMICS

To complete our discussion, we must now consider the possible consequences of relativistic thermodynamics. The technical modifications in thermodynamic theory needed to secure its extension to relativity may have seemed too trivial and obvious to warrant the expectation that these consequences could be very novel or interesting. Nevertheless, the actual effect of replacing classical ideas as to the nature of space and time by relativistic ideas is so fundamental as to lead to important differences between the results of classical and relativistic thermodynamics. Three examples may now be given to illustrate both the essential novelty and the inherent rationality of the consequences of relativistic thermodynamics.

(*a*) *Temperature Gradient in Gravitational Field.* In the classical thermodynamics we have become accustomed to the conclusion that a system which is in thermal equilibrium will necessarily have uniform temperature throughout. As a result of relativistic thermodynamics, however, it is found that this conclusion must be modified in the presence of appreciable gravitational fields. Thus if we consider a spherical distribution of material held together in static equilibrium by its own gravitational forces, corresponding to the line element,

$$ds^2 = -e^{\mu}\,(dr^2 + r^2 d\,\theta^2 + r^2 \sin^2\theta\, d\,\phi^2) + e^{\nu} dt^2 \qquad (23)$$

where μ and ν are functions of r alone, it can be shown[8] that the condition for thermal equilibrium is given by

$$\frac{d \log T_0}{dr} = -\tfrac{1}{2}\frac{d\nu}{dr} \qquad (24)$$

where T_0 the proper temperature as measured by a local observer decreases as we go outward instead of remaining constant. And for the more general static case of a system, not necessarily having spherical

[8] Tolman, *Phys. Rev.*, 35: 906, 1930.

symmetry, but corresponding to the more general line element

$$ds^2 = g_{ij}\,dx^i dx^j + g_{44}dt^2 \qquad (i, j = 1, 2, 3) \qquad (25)$$

where g_{ij} and g_{44} are independent of t, it has been shown by Professor Ehrenfest and myself[9] that the condition for thermal equilibrium would be given by a constant value throughout the system for the product

$$T_0 \sqrt{g_{44}} = \text{const} \qquad (26)$$

rather than for the proper temperature T_0 itself.

From an observational point of view, this new conclusion may not be very important, since the change in temperature with position would only be

$$\frac{d \log T}{dr} = 10^{-17}\ \text{cm}^{-1} \qquad (27)$$

in a gravitational field having the intensity of that at the earth's surface. From a theoretical point of view it is of interest, however, in leading to a modification of one of the most cherished results of the classical thermodynamics.

It should be emphasized, nevertheless, that this modification is entirely reasonable from the point of view of relativity. In accordance with that theory all forms of energy have mass and weight, and it is hence indeed not surprising that a temperature gradient is necessary to prevent the flow of heat from regions of higher to those of lower gravitational potential when thermal equilibrium has been reached. Furthermore, since the pressure of black-body radiation in equilibrium with a thermal system would evidently have to increase as we go to lower gravitational levels, in order to support the weight of radiation above, we can also see from purely mechanical considerations that temperature must increase with depth.

(*b*) *Possibility for Reversible Processes at a Finite Rate.* To turn to a second example, we have long been accustomed to believe as a result of the classical theory that *reversible* thermodynamic processes taking place at a *finite rate* could never occur in nature, since a finite rate of change would make it impossible to achieve that maximum efficiency which would permit a restoration both of the system and its surroundings to their original states.

To illustrate this we may consider a fluid contained in a cylinder with non-conducting walls and provided with a piston as shown in Fig. 1. The *reversible* expansion of this fluid with the piston moving out at a *finite rate* would evidently be impossible, in the first place since there would be friction between the piston and the walls, and in the second place since the fluid in flowing in behind the moving piston would not be able to maintain as high a pressure and hence do as much external work as at an infinitesimal rate of expansion. It has hence been concluded in the past that the reversible expansion of a fluid at a finite rate would under all circumstances be impossible.

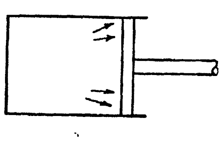

Fig. 1. Classical cylinder

[9] Tolman and Ehrenfest, *Phys. Rev.*, 36: 1791, 1930.

In relativistic thermodynamics, nevertheless, this situation is altered in an important manner by new possibilities for changes to take place in the proper volume of an element of fluid, because of changes in the gravitational potentials which were neglected in the older theory. To illustrate this, Fig. 2 attempts

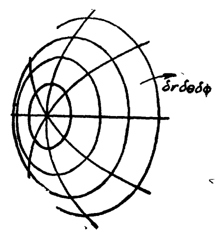

Fig. 2. Relativistic non-static universe

to give a symbolic two-dimensional representation of the space-like coordinates, corresponding to the line element

$$ds^2 = -\frac{e^{g(t)}}{\left[1 + \frac{r^2}{4R^2}\right]^2}\left(dr^2 + r^2\,d\theta^2 + r^2 \sin\theta\,d\phi^2\right) + dt^2 \qquad (28)$$

which characterizes the homogeneous distribution of fluid, that we usually call a non-static model of the universe. These coordinates are so selected that any element of fluid lying in a given coordinate range $\delta r\ \delta\theta\ \delta\phi$ will remain permanently therein. The proper volume of such an element of the fluid as measured by a local observer will then be

$$\delta V_0 = \frac{e^{\frac{3}{2}g(t)}}{\left[1 + \frac{r^2}{4R^2}\right]^3} r^2 \sin\theta\,\delta r\,\delta\theta\,\delta\phi \qquad (29)$$

and this will change with the time t at a finite rate on account of the occurrence of the function g(t) in the gravitational potentials and hence also in the expression for proper volume.

These changes in proper volume take place, however, in the first place quite obviously without any friction of moving parts, and in the second place with a perfect balance between internal and external pressures owing to the uniformity of conditions throughout the fluid. Thus the two sources of irreversibility in the previous classical illustration are completely eliminated. Furthermore, there can be no irreversible heat flow in the model under consideration, again owing to the uniform conditions throughout the fluid and the possibility of irreversible processes within each element of the fluid can be eliminated by the choice of a sufficiently simple substance. As a consequence it has proved possible to construct conceptual models of this kind[10] which can expand or contract at a finite rate, and nevertheless satisfy the relativistic condition for reversibility by maintaining the sign of equality instead of inequality in the simple expression

$$\frac{d}{dt}(\phi_0 \, \delta V_0) \geqq 0 \qquad (30)$$

which results from the application of the general form of the relativistic second law (19) to the present case.

This possibility for reversible thermodynamic processes taking place at a finite rate seems very strange from the point of view of the classical thermodynamics. Nevertheless, from the relativistic point of view the result seems both rational and, indeed, perhaps inevitable, when we recall that the principles of *relativistic mechanics* alone, without bothering about thermodynamics, have been found sufficient to show[11] the possibility of constructing models of the kind in question, which—when filled with such simple fluids as a perfect monatomic gas or black-body radiation—would expand at a finite rate to an upper limit and then precisely retrace their steps to their original density, pressure and temperature.

(*c*) *Possibility for Irreversible Processes without Reaching a Final State of Maximum Entropy.* As a final example of the differences between classical and relativistic thermodynamics, let us now turn to the classical conclusion that the ultimate result of irreversible processes taking place in a system having no interaction with its surroundings would necessarily be a state of maximum entropy where further change would be impossible.

To illustrate the classical reasons for belief in this principle, let us consider a simple homogeneous system consisting of a gas of uniform pressure, temperature, and composition throughout. The state of such a system can be specified by its energy E, volume v, and the number of mols N_1, N_2, etc., of the different chemical substances which it contains, and in accordance with a fundamental expression, provided by the work of Gibbs himself,[12] its entropy can then be determined with the help of the general equation

$$dS = \frac{dE}{T} + \frac{p}{T}dv + \left(\frac{\partial S}{\partial N_1}\right) dN_1 + \left(\frac{\partial S}{\partial N_2}\right) dN_2 + \ldots \qquad (31)$$

In applying this expression, however, to the special case of a system having no interaction with its surroundings, it was necessary in the classical thermodynamics to take the energy change dE equal to zero to agree with the classical principle of energy conservation. It was also necessary, for a system having no interaction with its surroundings, to take either the volume-change dv equal to zero or the pressure p itself equal to zero to prevent the performance of work on the surroundings. In both cases the only chance for entropy increase and hence for change would then lie in the readjustment of chemical composition. At constant energy and volume, moreover, this would have to cease when the entropy reached the maximum possible value compatible with the fixed value of energy and volume; while at constant energy and zero pressure the gas would be infinitely dilute and a final state of maximum entropy would be reached when all the molecules of gas had disassociated into their atoms.

In the relativistic treatment of this problem, nevertheless, the application of relativistic mechanics alone is sufficient to show a very different state of affairs. In the relativistic treatment, the analogue of the preceding homogeneous isolated system will evidently be a non-static model of the universe, since the line element for these models corresponds to a completely homogeneous distribution of fluid with no interaction with anything outside the system itself. By the application of relativistic mechanics, however, it has been shown by the work of Professor Ward and myself,[13] that there is a great class of such models, obtained by taking the cosmological constant Λ equal to zero or less, which could apparently undergo a continued succession of expansions and contractions without ever coming to rest. To be sure, the equations that we now have available for our highly idealized models are only sufficient to describe the expansion of the models to their upper limit and return, and not sufficient to describe their passage through the exceptional point at their lower limit of volume. Nevertheless, on physical grounds we must be inclined to assume that contraction to the lower limit of volume would be followed by renewed expansion.

It is to be specially noted now, however, that our conclusion as to the possibility of such behavior is based solely on mechanical equations alone and is quite independent of assumptions as to the reversibility or irreversibility of any thermodynamic processes that may take place in the fluid, although in the case of irreversible processes it can be shown that successive expansions have a tendency to go to larger and larger volumes before returning. The possibility thus

[10] Tolman, *Phys. Rev.*, 37: 1639, 1931; *ibid.*, 38: 797, 1931.

[11] Einstein, Berl. Ber. (1931) p. 235; Tolman, *Phys. Rev.*, 38: 1758, 1931.

[12] Allowing for the difference in notation and form, equation (31) is equivalent to the fundamental equation (12) given in the "Collected Works of Gibbs." Vol. I, p. 63. Longmans, Green and Company, 1928.

[13] Tolman, *Phys. Rev.*, 39: 320, 1932; Tolman and Ward, *ibid.*, 39: 835, 1932.

provided for an unending succession of irreversible expansions and contractions seems very strange from the point of view of classical thermodynamics, but can nevertheless be shown to be reasonable from the point of view of relativistic thermodynamics.

The application of the relativistic second law to these non-static models leads to the general result

$$\frac{d}{dt_0}(\phi_0 \, \delta V_0) \geqq 0 \qquad (32)$$

which states that the proper entropy of each element of the fluid as measured by a local observer can only remain constant or increase with local time. With a fluid of composition simple enough to eliminate the possibility for changes other than in density, we obtain the conditions necessary for constant entropy, and are led to the reversible expansions and contractions at a finite rate previously considered. With a slightly more complicated fluid, such as a gas which tends to disassociate as the density is lowered, we can obtain the irreversible increases in entropy in which we are now interested, since the composition of the fluid will then lag behind the changes in volume, and the processes of disassociation and recombination will always take place in the direction of an equilibrium which has not been attained.

From a classical point of view, such a continuous irreversible increase in entropy in an isolated system which undergoes a never-ending succession of expansions and recontractions to an earlier volume might seem impossible, since the energy of the isolated system would have to remain constant, and with a given value of energy and volume there would be a definite, maximum possible value of entropy.

From the relativistic point of view, nevertheless, it is easy to see that this continued increase in entropy could be made possible by the failure in relativistic mechanics of the ordinary principle of energy conservation. Indeed the application of relativistic mechanics to the models in question leads to the result

$$\frac{d}{dt_0}(\rho_{00} \, \delta V_0) + p_0 \frac{d}{dt_0}(\delta V_0) = 0 \qquad (33)$$

which shows that the proper energy $(\rho_{00} \, \delta V_0)$ of each element of fluid in the model will decrease as the model expands and increase as it contracts, and since the general effect of irreversibility would be to give higher pressures during compression than during the preceding expansion, we are thus provided with the needed mechanism for a gradual increase in proper energy and hence also in the proper entropy of the elements of fluid.

The difference between the classical and relativistic points of view can also be illustrated in a somewhat different manner, if we return to the classical cylinder and relativistic model of the universe given by Figs. 1 and 2, and consider a continued succession of expansions and contractions, in both cases providing for irreversibility by again introducing for example a gas which tends to disassociate when the pressure is lowered.

The classical man who is engaged in moving the piston of his cylinder successively in and out reports that the entropy inside the cylinder is all the time getting greater and greater, because the gas can not disassociate fast enough on the way out nor recombine fast enough on the way in to maintain equilibrium. He also reports, however, that the energy inside his cylinder—which is now no longer an isolated system—is also getting greater and greater, since the pressure has a tendency to be too high to correspond to equilibrium on compression and too low on expansion, so that he does more work on the way in than he gets back on the way out. He then finally remarks that this continued increase in energy indeed provides in the case of this non-isolated system an opportunity for the entropy to go on increasing forever, but that he personally is getting very tired of the silly experiment, and is going to have to stop:—not now because the irreversible processes will ever lead to an unsurpassable maximum of entropy but because he actually won't have the necessary energy to push in the piston one time more.

How different the remarks of the relativistic man as he sits calmly by and—in his mind's eye—watches his conceptual model expand and contract. "Yes," he says, "I notice that the proper entropy of each element of fluid is all the time increasing owing to successive processes of disassociation and recombination under conditions that do not correspond to equilibrium." "I do not worry, however, since I also notice that the proper energy of each element of fluid is also increased after a succession of expansions and contractions sufficiently to allow for this increase in entropy, and I know that the principles of relativistic mechanics not only permit such increases in proper energy, but indicate—without reference to reversibility or irreversibility—the continued succession of expansions and contractions that I observe."

This completes the discussion of examples illustrating the kind of conclusions that we may expect from the extension of thermodynamics to general relativity.

(6) Conclusion

Much remains to be done in the further application and development of relativistic thermodynamics. The application to systems in which heat flow is taking place from one portion of the fluid to another has not yet been undertaken and might lead to interesting results. It could be of special importance when we have made more progress in the treatment of nonhomogeneous models of the universe which may well be necessary for a better understanding of the actual universe. The development of relativistic thermodynamics to include an appropriate treatment of fluctuations might also be attempted with the help of the statistical methods introduced by Gibbs himself. The effect of fluctuations on the behavior of cosmological models might be specially important at certain stages of their history.

In trying to estimate the significance of the applications of relativistic thermodynamics that have already been made, we must not misjudge the nature of the two applications to cosmological models that were described in the foregoing. It should be emphasized that the homogeneous cosmological models which we now consider are not only very highly simplified and idealized, but at best are constructed to agree throughout their entire extent with that small sample of the actual universe which lies within the range of some 10^8 light years. Furthermore, it must be remembered that among the different possible kinds of homogeneous cosmological model, there is a class which would expand never to return as well as the class that could undergo an unending succession of expansions and contractions; and we do not now have sufficient data so that we could assign the actual universe to either class. Hence we must be very careful, in extrapolating to the actual universe any conclusions that we may draw as to the behavior of our conceptual models.

The dangers of long-range extrapolation were specially emphasized to you by Professor Bridgman in his beautiful Gibbs memorial lecture of last year, and these dangers, as we see, are specially present in cosmological speculations, based on the observation of a small fragment of the total universe for an inappreciable time span. Nevertheless, it certainly seems significant that conceptual models of the universe can be constructed, which are permitted by the principles of relativistic thermodynamics to exhibit behavior in serious conflict with the classical conclusions, that reversible processes could never take place at a finite rate, and that the end result of irreversible processes would necessarily be a stationary condition of maximum entropy. Hence at the very least it would now seem desirable to extrapolate to a cautious position, in which we no longer dogmatically assert that the principles of thermodynamics necessarily require a universe created at a finite time in the past and fated for stagnation and death in the future. Indeed, the chief duty and glory of theoretical science is certainly, not merely to describe in complicated language those facts that are already known, but to extrapolate—as cautiously and wisely as may be—into regions yet unexplored but pregnant with human interest.

ACTIVE IRON

By Dr. OSKAR BAUDISCH

DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY

IN the year 1806 the Bergrat Johann Georg Lenz named a natural iron oxide hydrate "goethite," in honor of the celebrated naturalist and poet, Johann Wolfgang von Goethe. This mineral had already been known in the literature previously under the name ruby mica (Rubinglimmer).[1] Although comparatively rare, it is found in good crystalline form in Siegen, in Westphalia. The splendid crystals, one to two millimeters long, indeed resemble rubies in their beautiful color and luster. The crystals or powder made from them are non-magnetic, but if one dehydrates the powder by heating it a magnetic iron oxide, Fe_2O_3, is obtained. This interesting observation was described as early as 1838 in the book "Grundzüge der Mineralogie" by Franz von Kobel (published in Nürnberg in 1838). The names ruby mica and goethite are used interchangeably for this macro-crystalline brown iron ore in the "Manual of Mineralogy" by Robert Allan (Edinburgh, 1834). It is seen, therefore, that historically the names ruby mica and goethite properly apply to the natural iron oxide hydrate which becomes magnetic on heating.

In the year 1848, Plücker made a magnetic study of the natural and artificial iron oxides and oxide hydrates, and observed that an iron oxide hydrate prepared in a certain way gave a magnetic iron oxide on dehydration. He found it almost a hundred times stronger magnetically than the original hydrate from which it was prepared, and remarked that the powdered material could be picked up by even a small horseshoe magnet. Robbins mentioned a magnetic iron oxide in *Chemical News* in the year 1859.

Malaguti in 1863 (*Compte Rendus*) published more exact chemical and physical data on the properties of magnetic iron oxide. He obtained the oxide in various ways, as, for example, by explosion of magnetite with potassium chlorate and by heating ferrous salts of organic acids in the air. In France the magnetic iron oxide is also known under the name Malaguti-oxide.

[1] J. F. L. Hausman, "Handbuch der Mineralogie," Göttingen, 1813.