

<sup>8</sup> Cf. Millikan, R. A., *The Electron: Its Isolation and Measurement and the Determination of Some of Its Properties*, Chicago, University of Chicago Press, 1917, 260 pp.

<sup>9</sup> We may cite the recent experiments of Davisson, C., and Germer, L. H., "On the Diffraction of Cathode-Rays by Crystals," *Physic. Rev.*, **30** (1927), pp. 705-741. Equally relevant is the work of F. Kirchner, on the "Compton Effect as Manifested by Individual Electrons," *Ann. Physik*, **83** (1927), pp. 969-76.

<sup>10</sup> Cf. Bohr, N., Kramers, H. A., und Slater, J. C., "Über die Quantentheorie der Strahlung," *Zs. Physik*, **24** (1924), pp. 69-88. Here a theory of the relation of light quanta to light waves is developed which invites comparison with that developed in the present paper.

<sup>11</sup> Struik, D. J., and Wiener, N., "A Relativistic Theory of Quanta," *J. Math. Phys. Mass. Inst. Tech.*, **7** (1927-28), pp. 1-23.

<sup>12</sup> For a discussion of the constancy of  $\gamma_{00}$ , see Einstein, A., "Zu Kaluzas Theorie des Zusammenhanges von Gravitation und Elektrizität," *Sitzungsber. Berlin Akad.*, 1927. Erste Mitteilung, pp. 23-25, 26-30.

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## ON THE EXTENSION OF THERMODYNAMICS TO GENERAL RELATIVITY

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Communicated January 3, 1928

1. *Introduction.*—The recent interesting article of Lenz<sup>1</sup> on the equilibrium between radiation and matter in Einstein's closed universe makes it desirable to investigate the proper method of extending the ordinary principles of thermodynamics so as to make them hold for considerations in curved space-time where the methods of general relativity must be employed.

The considerations of Lenz were apparently based on principles borrowed with little modification from the ordinary thermodynamics valid in flat space-time. Thus the condition of equilibrium in the universe was assumed to be maximum entropy for variations which did not affect the total energy, and the expressions used for energy and entropy differed from those known to hold in flat space-time merely by the substitution of a quantity representing a volume of curved three-dimensional space in place of an ordinary volume of flat space. Since it is well known, however, that in curved space-time it is, in general, a matter of considerable difficulty to find any suitable expression for energy,<sup>2</sup> and since hitherto, as far as I am aware, no investigations have been made as to a proper general relativity expression for entropy, it is evident that Lenz's treatment does not provide a general nor necessarily a correct method of attacking thermodynamic problems in curved space-time.

It is the purpose of the present article to consider two principles expressed in the form of equations true for all sets of coördinates which may serve as the analogues in general relativity of the ordinary first and second laws of thermodynamics.

In a following article, I then hope to consider the problem of Lenz.

2. *The First Law.*—As the first law for our system of thermodynamics we must evidently take the analogue in general relativity of the law of the conservation of energy. This analogue, which in flat space-time leads to the conservation of energy and also of momentum, is given as is well known by the tensor equation<sup>3</sup>

$$(T_{\mu}^{\nu})_{;\nu} = 0 \tag{1}$$

where  $T_{\mu}^{\nu}$  is the total energy tensor for matter and electricity.

In order to make use of equation (1), it will be convenient to change to tensor densities and integrate. To do this, equation (1) can be rewritten in the form<sup>4</sup>

$$\mathfrak{T}_{\mu\nu} = (T_{\mu}^{\nu})_{\nu} \sqrt{-g} = \frac{\partial \mathfrak{T}_{\mu}^{\nu}}{\partial x_{\nu}} - \frac{1}{2} \mathfrak{T}^{\alpha\beta} \frac{\partial g_{\alpha\beta}}{\partial x_{\mu}} = 0. \tag{2}$$

By integration over a definite four-dimensional region, we then obtain

$$\int \int \int \int \left( \frac{\partial \mathfrak{T}_{\mu}^{\nu}}{\partial x_{\nu}} - \frac{1}{2} \mathfrak{T}^{\alpha\beta} \frac{\partial g_{\alpha\beta}}{\partial x_{\mu}} \right) dx_1 dx_2 dx_3 dx_4 = 0. \tag{3}$$

This equation is evidently valid for all sets of coördinates and can be used as the starting point for energy (and momentum) investigations.

3. *The Second Law.*—Taking equation (3) as a suitable analogue in general relativity for the ordinary first law of thermodynamics, we must now try to discover a proper expression for the second law of thermodynamics.

Here we are on quite new ground. We have, however, two principles to guide us: In the first place our postulate must be expressible in a form which is true for all systems of coördinates; and in the second place the postulate must be equivalent to the ordinary second law of thermodynamics for the case of flat space-time. These requirements, simple as they seem, are stringent enough to lend considerable probability to any postulate that fulfills them.

To express the postulate that we have chosen as satisfying the conditions we shall first define the *entropy vector* at any given point in space-time by the equation

$$S^{\mu} = \phi_0 \frac{dx_{\mu}}{ds} \tag{4}$$

where  $dx_{\mu}/ds$  refers to the macroscopic motion of the matter (or energy)

at the point in question and  $\phi_0$  is the proper density of entropy as measured by an observer moving with that matter.

Taking the divergence of  $S^\mu$  and multiplying by  $\sqrt{-g}$  to prepare for integration we obtain<sup>5</sup>

$$(S^\mu)_\mu \sqrt{-g} = \mathfrak{E}_\mu^\mu = \frac{\partial \mathfrak{E}^\mu}{\partial x_\mu}. \quad (5)$$

If we consider now the integral of (5) over a four-dimensional region which includes the whole of any isolated thermodynamic system,<sup>6</sup> our postulate will be given by the equation

$$\iiint \int \frac{\partial \mathfrak{E}^\mu}{\partial x_\mu} dx_1 dx_2 dx_3 dx_4 \geq 0 \quad (6)$$

under the condition

$$\iiint \int \left( \frac{\partial \mathfrak{E}^\mu}{\partial x_\mu} - \frac{1}{2} \mathfrak{T}^{\alpha\beta} \frac{\partial g_{\alpha\beta}}{\partial x_\mu} \right) dx_1 dx_2 dx_3 dx_4 = 0. \quad (7)$$

4. *Tests of the Postulate.*—We must now examine our postulated equations to see if they meet the necessary requirements.

Looking first at equation (6), we note that  $(S^\mu)_\mu$  and  $\sqrt{-g} dx_1 dx_2 dx_3 dx_4$  are both of them invariants so that the equation itself is a tensor equation of rank zero. Turning now to equation (7), although the integral involved is not a tensor since the integration is taken over a finite region, nevertheless, as shown in the preceding section, the equation is true for all sets of coördinates. Hence, our postulated equations do fulfill the first of the requirements, namely, that of covariance, which we laid down above.

To show that they reduce to the known principles of thermodynamics in flat space-time, we must consider the significance of these equations in the Galilean coördinates which can then be used.

For Galilean coördinates  $x, y, z, t$ , we have

$$\sqrt{-g} = 1 \quad (8)$$

and referring to the equation of definition (4), can write for the entropy vector

$$\begin{aligned} \mathfrak{E}^\mu = S^\mu &= \left( \phi_0 \frac{dx}{ds}, \phi_0 \frac{dy}{ds}, \phi_0 \frac{dz}{ds}, \phi_0 \frac{dt}{ds} \right) \\ &= \left( \phi_0 \frac{dt}{ds} \frac{dx}{dt}, \phi_0 \frac{dt}{ds} \frac{dy}{dt}, \phi_0 \frac{dt}{ds} \frac{dz}{dt}, \phi_0 \frac{dt}{ds} \right). \end{aligned} \quad (9)$$

Since, however, on account of its relation to probability, the entropy of an infinitesimal region in flat space-time is known to be an invariant for the Lorentz transformation, entropy density will be so related to the Lorentz-

Fitzgerald factor of contraction  $ds/dt$  that we can rewrite equation (9) in the form

$$\mathfrak{E}^\mu = (\phi u, \phi v, \phi w, \phi) \tag{10}$$

where  $\phi$  is the density of entropy and  $u, v$  and  $w$  are the components of macroscopic velocity in the system of coördinates that we are now using.

We then have in these coördinates

$$\frac{\partial \mathfrak{E}^\mu}{\partial x_\mu} = \frac{\partial}{\partial x} (\phi u) + \frac{\partial}{\partial y} (\phi v) + \frac{\partial}{\partial z} (\phi w) + \frac{\partial \phi}{\partial t} \tag{11}$$

and it is easy to show that the integral of this expression over a three-dimensional isolated volume gives the rate of production of entropy inside the boundary. So that for an isolated system our postulate, equation (6), will reduce in flat space-time to

$$\int_t^{t'} \frac{dS}{dt} dt = (S' - S) \geq 0 \tag{12}$$

where  $S$  and  $S'$  are the total entropies of the system at times  $t$  and  $t'$ .

It is also immediately evident, moreover, from the known value of the energy tensor in flat space-time that equation (7) will reduce for the case  $\mu = 4$  to the expression

$$U' - U = 0 \tag{13}$$

where  $U$  is the total energy of our isolated system. Equations (12) and (13), however, are the accepted expressions for the thermodynamics of an isolated system in flat space-time. Hence, our postulates also fulfill the second of the two necessary requirements, namely, of reducing to ordinary thermodynamics in flat space-time.

5. *Remarks on the Postulates.*—In conclusion, certain remarks concerning the nature of the postulates will not be out of place.

In order to apply the first law of thermodynamics, as given by equation (3) (7), it will often be more convenient to express the second term of the integrand as a function of the components of the fundamental tensor and its derivatives. This permits us to rewrite the equation in the often more useful form

$$\int \int \int \int \left( \frac{\partial \mathfrak{T}_\mu^\nu}{\partial x_\nu} + \frac{\partial t_\mu^\nu}{\partial x_\nu} \right) dx_1 dx_2 dx_3 dx_4 = 0 \tag{14}$$

where  $t_\mu^\nu$ , the so-called pseudo-tensor of gravitational energy, is a known, though complicated, function of the  $g_{\mu\nu}$ 's and their differential coefficients. Equation (14) like the equivalent equations (3) (7) is, of course, not a tensor equation, but nevertheless is true in all sets of coördinates.

With regard to the second law of thermodynamics, as given by equation (6), it should be noted that the sign "is greater than" applies to the case of a system which is approaching the condition of thermodynamic equilibrium and implies a difference between "forward" and "backward" directions for the time-like coordinate  $x_4$ . The equality sign, on the other hand, may characterize either a system which is in a condition of thermodynamic equilibrium, or one in which changes in the direction of equilibrium are not taking place. To distinguish the important case of thermodynamic equilibrium from one of mere delayed change is usually not difficult, since it is merely necessary to see if zero is the maximum possible value for the integral in equation (6).

<sup>1</sup> Lenz, W., *Physik. Z.*, 27, 1926 (642-645).

<sup>2</sup> Einstein, A., *Sitz. Ber. Preuss. Akad.*, 1918 (448-459).

<sup>3</sup> See, for example, Eddington, *The Mathematical Theory of Relativity*, Cambridge, 1923, equations 54.22 and 76.3.

<sup>4</sup> For the reduction see Eddington, l. c., equations 51.31 and 51.51.

<sup>5</sup> For the reduction see Eddington, l. c., equations 51.11 and 51.12.

<sup>6</sup> In the immediately following we shall regard the universe as a whole as an isolated system. I hope to give a further elucidation of this point at a later time.

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*ON THE VARIATION OF THE ELECTROMOTIVE FORCE IN A  
PHOTOACTIVE CELL, CONTAINING A FLUORESCENT  
ELECTROLYTE, WITH THE INTENSITY OF ILLUMINATION*

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Communicated February 4, 1928

*Introduction.*—When two similar electrodes are immersed in a suitable solution and one of the electrodes is illuminated, the other being kept in the dark, an e.m.f. is produced which varies with the time of illumination. On cutting off the illumination this e.m.f. decreases with time. The effect is well shown using fluorescent solutions such as rhodamine, eosin and fluorescein.

The e.m.f. was first attributed by Goldmann<sup>1</sup> and others to a photoelectric effect, electrons being set free from the photosensitive molecules. Recent work, however, by Perrin<sup>2</sup> and Wood<sup>3</sup> on the photochemical changes produced in fluorescent solutions by illumination, lead one to believe that the e.m.f. owes its origin, in great part, to such photochemical modification of the fluorescent electrolyte as would take place at the illuminated electrode. The e.m.f. can then be attributed to the increase in concentration of the new material or materials formed in the neighbor-