The Thermodynamics of Irreversible Processes

III. Relativistic Theory of the Simple Fluid

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The considerations of the first paper of this series are modified so as to be consistent with the special theory of relativity. It is shown that the inertia of energy does not obviate the necessity for assuming the conservation of matter. *Matter* is to be interpreted as number of molecules, therefore, and not as inertia. Its velocity vector serves to define local proper-time axes, and the energy momentum tensor is resolved into proper-time and -space components. It is shown that the first law of thermodynamics is a scalar equation, and not the fourth component of the energy-momentum principle. Temperature and entropy also prove to be scalars. Simple relativistic generalizations of Fourier's law of heat conduction, and of the laws of viscosity are obtained from the requirements of the second law. The same considerations lead directly to the accepted relativistic form of Ohm's law.

INTRODUCTION

IN the second paper of this series,[1] the theory of ϵ-substitutions was outlined, and it was shown that this device can be used to simplify the derivation of some thermodynamic formulae. However, the author was reluctant to use it in the derivation of any fundamental formulae because the ϵ-substitution depends on the fact that the internal energy contains an arbitrary additive constant, while the principle of the equivalence of mass and energy appears to give an absolute meaning to the energy content of any portion of matter. Thus it seemed possible that in a relativistic theory of thermodynamics, ϵ-substitutions might be inadmissible. The considerations which follow show that this is not the case. To establish this result, it was necessary to develop a complete relativistically invariant theory of the simple fluid—a project which is of interest in itself, even though the departures of such a theory from a classical theory must be negligible in most cases.

In I, four general principles were used: (a) The conservation of matter; (b) the conservation of momentum; (c) the conservation of energy; and (d) Kelvin's hypothesis concerning the thermodynamic temperature. It might seem as though the equivalence of mass and energy would make (a) superfluous in a relativistic theory. This is not the case, as becomes clear if *matter* is interpreted as number of molecules rather than inertia. The principles (b) and (c) combine into a single tensor equation, as is well known. This is somewhat disconcerting, for the first law of thermodynamics is a scalar equation; its relation to the energy-momentum principle must be discovered. Moreover, the correct form of the energy-momentum tensor is still a matter of discussion, and some assumption must be made before the theory can be completed. Finally, Kelvin's hypothesis involves Fourier's law of heat conduction, and the relativistic generalization of this presents a difficulty, arising from the fact that in the classical theory there is a three-vector that represents the flow of heat, but no density of heat to combine with it to form a four-vector. A somewhat similar difficulty arises in connection with the stress-tensor.[2] It will be shown that all of these problems can be solved in a systematic manner if one defines proper-time and proper-space in terms of the velocity of matter.

MATTER, PROPER-TIME, AND PROPER-SPACE

A Galilean coordinate system ($x^0=ct$, x^1, x^2, x^3) will be assumed, in which the metric tensor is

$$g^{\alpha\beta}=\begin{matrix}-1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{matrix} \tag{1}$$

[1] C. Eckart, Phys. Rev. **58**, 267, 269 (1940); hereafter cited as I and II, respectively.

[2] R. C. Tolman has solved this problem for the stresses; see his *Theory of the Relativity of Motion* (University of California Press, 1918), Chap. X, and *Relativity, Thermodynamics and Cosmology* (Oxford, 1934), Chap. III.

and this tensor will be used to raise and lower indices in the usual manner. Matter will be represented by a four-vector, m^α, which has the units g/cm^3, and depends only on the molecular weight and on the motion of the molecules. The inertia and internal energy of the molecules will be introduced later, so that the molecular weight is to be considered only as a convenient conversion factor. The conservation of matter is expressed by the equation

$$\partial m^\alpha/\partial x^\alpha = 0. \qquad (2)$$

It is to be assumed that $m^0 > 0$, and that the invariant density

$$m = (-g_{\alpha\beta} m^\alpha m^\beta)^{\frac{1}{2}} \qquad (3)$$

is real and positive. The (dimensionless) velocity of matter is

$$u^\alpha = m^\alpha/m, \qquad (4)$$

so that

$$u_\alpha u^\alpha = -1 \qquad (5)$$

and

$$u^\alpha(\partial u_\alpha/\partial x^\beta) = u_\alpha(\partial u^\alpha/\partial x^\beta) = 0. \qquad (6)$$

The vector u^α will be a function of the coordinates, and will determine a direction at each point of four-space—the local axis of proper-time. Three directions orthogonal to this are the local axes of proper space. Any vector F^α, then gives rise to a scalar and a vector by means of the equations

$$f = -u_\alpha F^\alpha, \qquad (7)$$

$$f^\alpha = s_\beta{}^\alpha F^\beta, \qquad (8)$$

$$s_\beta{}^\alpha = \delta_\beta{}^\alpha + u^\alpha u_\beta. \qquad (9)$$

The scalar f is the projection of F^α on the axis of proper-time, and f^α is the projection of F^α into proper-space. It is easily seen that

$$F^\alpha = f u^\alpha + f^\alpha$$

and that

$$u_\alpha s_\beta{}^\alpha = 0, \quad u^\beta s_\beta{}^\alpha = 0. \qquad (10)$$

Covariant vectors can be resolved into proper components in an analogous manner.

The tensor $s_\beta{}^\alpha$ has several important properties: it is easily seen that

$$s_\beta{}^\alpha s_\gamma{}^\beta = s_\gamma{}^\alpha \qquad (11)$$

and

$$s^{\alpha\beta} = s_\gamma{}^\alpha g^{\gamma\beta} = g^{\alpha\beta} + u^\alpha u^\beta \qquad (12)$$

is a symmetric tensor. A simple calculation shows that

$$s^{\alpha\beta} = s^{\alpha\gamma} s_\gamma{}^\beta = s_\delta{}^\alpha g^{\delta\gamma} s_\gamma{}^\beta, \qquad (13)$$

so that, because of Eq. (5),

$$s^{\alpha\beta} F_\alpha F_\beta = g^{\gamma\delta} f_\gamma f_\delta \geqslant 0, \qquad (14)$$

the equality holding only when $F_\alpha = f u_\alpha$.

This resolution of vectors into time and space components is quite consistent with Einstein's theory of simultaneity, since there is no reference to separated points of four-space. This becomes clearer on defining the proper-rate of change of a quantity:

$$D\phi = u^\alpha(\partial\phi/\partial x^\alpha). \qquad (15)$$

This may be called the derivative of ϕ with respect to proper-time. However, proper-time itself has not yet been defined; one may try to define it by the equation

$$D\tau = 1$$

but this does not determine a unique function τ. To make τ unique, it is necessary to specify one surface in four-space on which $\tau = 0$, i.e., one locus of simultaneous events. The essence of Einstein's theory is that this locus cannot be specified in a physically unique manner, so that τ remains somewhat arbitrary. The differential operator D is unique, however, and corresponds closely to the classical operator D/Dt.

The Eq. (2) is readily transformed into

$$\partial u^\alpha/\partial x^\alpha = -vDm = mDv, \qquad (16)$$

where $v = 1/m$ is the invariant specific volume (cf. I, Eq. (2)). Equation (6) yields

$$u^\alpha D u_\alpha = u_\alpha D u^\alpha = 0. \qquad (17)$$

Resolution of the Energy-Momentum Tensor into Proper Components

The energy-momentum principle will be assumed in the usual relativistic form,

$$\partial W^{\alpha\beta}/\partial x^\alpha = 0, \quad W^{\alpha\beta} = W^{\beta\alpha}, \qquad (18)$$

the units of W being erg/cm^3.

The equation obtained by setting $\beta = 0$ in Eq. (18) is variously called the equation of conservation of matter, of mass or inertia, and of energy. It seems to the author that, while each of these designations can be justified in special cases, the first two are misleading in general. He would prefer to retain only the third, and refer to the equation $W^{\alpha 0}=W^{0\alpha}$ as the principle of the inertia of energy. Even the third is misleading unless a distinction is made between the principle of conservation of energy and the first law of thermodynamics, the two being identical only when matter is at rest (see below).

For the moment, no assumption will be made concerning the form of $W^{\alpha\beta}$, but it will be used in defining other quantities, such as the internal energy and heat flow. Assumptions concerning the form of these quantities will be made below.

The tensor W may be resolved into proper-components: if

$$w=W^{\alpha\beta}u_\alpha u_\beta, \tag{19}$$

$$w^\alpha=-s_\beta{}^\alpha W^{\beta\gamma}u_\gamma, \tag{20}$$

$$w^{\alpha\beta}=s_\gamma{}^\alpha s_\delta{}^\beta W^{\gamma\delta}, \tag{21}$$

then

$$W^{\alpha\beta}=wu^\alpha u^\beta+w^\alpha u^\beta+w^\beta u^\alpha+w^{\alpha\beta}. \tag{22}$$

It will appear that each of these components has an important physical interpretation. Thus, w is the invariant density of energy (erg/cm^3). The internal energy, ϵ (erg/g$=$cm^2/sec.^{2}), is appropriately defined by

$$m(\epsilon+a)=w, \tag{23}$$

a being an arbitrary constant. It will appear that a does not enter into the first law of thermodynamics. The vector

$$q^\alpha=cw^\alpha \tag{24}$$

is the heat flow in erg/cm^2 sec.; the equation

$$u_\alpha q^\alpha=0, \tag{25}$$

which follows from Eq. (10) and (20), corresponds to the absence of a density of heat in the classical theory. The symmetric tensor $-w^{\alpha\beta}$ is the stress tensor (dynes/cm^2); the equation

$$u_\alpha w^{\alpha\beta}=0 \tag{26}$$

reduces the number of its independent components to six, as in the classical theory.

The First Law of Thermodynamics

The first law of thermodynamics can be derived from Eq. (18) and the definitions just adopted. Multiplying Eq. (18) scalarly by $-u_\beta$ and rearranging, we have

$$-(\partial/\partial x^\alpha)(u_\beta W^{\alpha\beta})+W^{\alpha\beta}(\partial u_\beta/\partial x^\alpha)=0; \tag{27}$$

because of Eqs. (19), (20), (22)

$$-u_\beta W^{\alpha\beta}=wu^\alpha+w^\alpha$$
$$=m(\epsilon+a)u^\alpha+q^\alpha/c.$$

Since $mu^\alpha=m^\alpha$, Eq. (2) results in the disappearance of a from the equation:[3]

$$-(\partial/\partial x^\alpha)(u_\beta W^{\alpha\beta})=(\partial/\partial x^\alpha)(m\epsilon u^\alpha+q^\alpha/c)$$
$$=mD\epsilon+(1/c)(\partial q^\alpha/\partial x^\alpha).$$

Equations (6) and (22) result in

$$W^{\alpha\beta}(\partial u_\beta/\partial x^\alpha)=w^\beta Du_\beta+w^{\alpha\beta}(\partial u_\beta/\partial x^\alpha),$$

so that finally Eq. (27) becomes

$$mD\epsilon+(1/c)[(\partial q^\alpha/\partial x^\alpha)+q^\alpha Du_\alpha]$$
$$+w^{\alpha\beta}(\partial u_\beta/\partial x^\alpha)=0. \tag{28}$$

This is to be compared with the classical form of the first law (cf. I, Eq. (7))

$$m(D\epsilon/Dt)+\nabla\cdot\mathbf{q}-(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}=0,$$

$\mathbf{q}$ being the heat flow, $\mathbf{V}$ the velocity and $\mathfrak{p}$ the total stress. The terms of the two equations are in an obvious correspondence, except that the term $(1/c)q^\alpha Du_\alpha$ does not appear in the classical case. This term is very small in all ordinary cases, and may be interpreted as the work done by a flow of heat through accelerated matter—a phenomenon not envisaged by the classical theory.

[3] It will be noted that, up to this point, the introduction of the matter vector, m^α, served no purpose except to define the density and velocity of matter, m and u^α. Tolman, reference 2, and others avoid introducing m^α, but cannot avoid introducing u^α. At this place in the considerations, however, it becomes important that matter be conserved (Eq. (2)). If this were not the case, the constant a would enter into the first law of thermodynamics, Eq. (28), in the form of a term $a(\partial m^\alpha/\partial x^\alpha)$. In other words, the creation or annihilation of matter requires energy absorption or release. This is as it should be, and indicates that the theory of ϵ-substitutions may be used even in relativistic considerations, except when matter is being created or destroyed. The theory of such nuclear processes is beyond the scope of the present paper, particularly insofar as electric charges and radiation are involved. Insofar as only heavy particles are involved, the device of using mass numbers (integers) in the definition of m^α (and thus including the packing-fraction energy in ϵ) will insure the validity of Eq. (2).

The Simple Fluid and the Second Law of Thermodynamics

The theory of the simple fluid is of considerable importance, since in this case it is possible to prove the existence of temperature and entropy (cf. I, Eq. (9) *et seq.*). The appropriate definition of the hydrostatic pressure is

$$p=\tfrac{1}{3}w_\alpha{}^\alpha \tag{29}$$

and it is to be assumed that the viscous stress tensor,

$$P^{\alpha\beta}=-w^{\alpha\beta}+ps^{\alpha\beta} \tag{30}$$

is a linear function of $(\partial u_\gamma/\partial x^\delta)$ and proportional to the scalar coefficient of viscosity, λ. This together with the equations

$$u_\alpha P^{\alpha\beta}=0,\quad P_\alpha{}^\alpha=0, \tag{31}$$

which follow from Eqs. (29) and (30), restricts the form of P very materially. The equation

$$P^{\alpha\beta}=\lambda c\{s^{\alpha\gamma}s^{\beta\delta}[(\partial u_\gamma/\partial x^\delta)+(\partial u_\delta/\partial x^\gamma)] -\tfrac{2}{3}s^{\alpha\beta}s^{\gamma\delta}(\partial u_\gamma/\partial x^\delta)\} \tag{32}$$

is very strongly indicated, if not uniquely determined. At any rate, this expression for P satisfies Eq. (31), and differs from the classical expression only by terms that are ordinarily negligible (see below).

Since

$$s^{\alpha\beta}(\partial u_\beta/\partial x^\alpha)=(\partial u^\alpha/\partial x^\alpha)=mDv$$

by Eqs. (6), (12), and (16), the Eq. (28) becomes

$$m(D\epsilon+pDv)+(1/c)[(\partial q^\alpha/\partial x^\alpha)+q^\alpha Du_\alpha] -P^{\alpha\beta}(\partial u_\beta/\partial x^\alpha)=0. \tag{33}$$

For the simple fluid, ϵ is a function of p and v only, so that there are two functions θ and η such that

$$D\epsilon+pDv=\theta D\eta; \tag{34}$$

the proof is identical with that given in I. Since ϵ, p and v are scalars, θ and η will also be scalars.[4] Substituting in Eq. (33) and rearranging, we obtain

$$mD\eta+(\partial/\partial x^\alpha)(q^\alpha/c\theta)=-(1/c\theta^2)q^\alpha[(\partial\theta/\partial x^\alpha) +\theta Du^\alpha]+(1/\theta)P^{\alpha\beta}(\partial u_\beta/\partial x^\alpha). \tag{35}$$

[4] The scalar character of η appears to be generally accepted (cf. Tolman, *Relativity of Motion*, Chap. XI). However, M. Planck introduced a nonscalar quantity, T, which he identified with temperature, and which appears to be related to the present θ by the equation $T=\theta u^0$. Tolman introduces a quantity T° which appears to be identical with θ.

The inequality

$$mD\eta+(\partial/\partial x^\alpha)(q^\alpha/c\theta)\geqslant 0 \tag{36}$$

cannot be proved without some assumption concerning the relativistic form of Fourier's law and Kelvin's hypothesis. The simplest assumption leading to Eq. (36) is that

$$q^\alpha=-ks^{\alpha\beta}[(\partial\theta/\partial x^\beta)+\theta Du_\beta], \tag{37}$$

which satisfies Eq. (25) and reduces to the classical Fourier's law when ordinarily negligible terms are canceled (see below). The scalar $k(\geqslant 0)$ is the thermal conductivity of the fluid. The term $s^{\alpha\beta}(\partial\theta/\partial x^\beta)$ is obviously the relativistic temperature gradient. The term $-\theta Du_\beta$ has no classical analog, and implies an isothermal flow of heat in accelerated matter, in the direction opposite to the acceleration. It is ordinarily small, and may be explained as due to the inertia of energy. Equation (37) shows that $q^\alpha=0$ when the vector $\partial\theta/\partial x^\beta+\theta Du_\beta$ is parallel to the proper-time axis. This seems strange at first, but on reflection, it is seen to correspond to the fact that, in the classical theory, there will be no flow of heat if $\nabla\theta=0$ even though $\partial\theta/\partial t\neq 0$—i.e., that there are adiabatic changes of temperature.

As was discussed in I, Eq. (34) does not determine θ and η uniquely; however, if it be assumed that Eq. (37) holds for two of the possible functions θ, θ_0 and all possible values of

$$s^{\alpha\beta}(\partial v/\partial x^\beta),\quad s^{\alpha\beta}(\partial p/\partial x^\beta),\quad s^{\alpha\beta}Du_\beta,$$

then it can be shown as in I that

$$\theta/\theta_0=\text{const.}$$

Thus Eq. (37) fixes the definition of the temperature except for a choice of unit.

From Eqs. (14) and (37), it follows at once that

$$-(1/c\theta^2)q^\alpha[(\partial\theta/\partial x^\alpha)+\theta Du_\alpha]\geqslant 0. \tag{38}$$

It therefore remains to show that

$$P^{\alpha\beta}(\partial u_\beta/\partial x^\alpha)\geqslant 0, \tag{39}$$

the positiveness of λ and θ being assumed. For this purpose, the attention may be fixed on a single arbitrary point, A, in four-space. If the time-axis of the Galilean coordinate system is chosen parallel to the proper-time axis at A, then at this point,

$$u^\alpha = 1, 0, 0, 0,$$
$$u_\alpha = -1, 0, 0, 0, \quad (40)$$

and

$$s^{\alpha\beta} = \begin{matrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1. \end{matrix} \quad (41)$$

Substitution into Eq. (32) shows that

$$P^{00} = P^{01} = \cdots = 0,$$

while

$$P^{11} = \tfrac{2}{3}\lambda c\{[(\partial u_1/\partial x^1) - (\partial u_2/\partial x^2)] + [(\partial u_1/\partial x^1) - (\partial u_3/\partial x^3)]\}, \quad (42)$$

$$P^{12} = \lambda c[(\partial u_1/\partial x^2) + (\partial u_2/\partial x^1)], \text{ etc.,}$$

which are the classical expressions for the viscous stresses. It then follows, as in I, that Eq. (39) is true at the point A, and thus everywhere in four-space.

The Momentum of Heat

The general principle of the inertia of energy leads one to expect that a flow of heat q will be associated with a momentum q/c^2. This result can be read out of the form of the energy-momentum tensor (Eqs. (22) and (24)), but it is interesting to consider the question in somewhat more detail. It will be supposed that the fluid is at rest in the Galilean system x^α, so that Eqs. (40) and (41) are valid at all points of four-space and $P^{\alpha\beta} = 0$. Then Eq. (37) yields

$$q^0 = 0$$
$$q^\kappa = -k\partial\theta/\partial x^\kappa, \quad \kappa = 1, 2, 3,$$

while Eq. (2) becomes

$$\partial m/\partial t = 0$$

so that m and v are functions of x^1, x^2, x^3 only. The components of the energy-momentum tensor are

$$W^{00} = m(\epsilon + a),$$
$$W^{0\kappa} = q^\kappa/c = W^{\kappa 0},$$
$$W^{\kappa\mu} = p\delta^{\kappa\mu}.$$

The Eqs. (18) become

$$m(\partial\epsilon/\partial t) + (\partial q^\kappa/\partial x^\kappa) = 0 \quad (43)$$

and

$$(\partial/\partial t)(q^\kappa/c^2) + (\partial p/\partial x^\kappa) = 0. \quad (44)$$

Equation (43) is the equation of conservation of energy, and is (in this case only!) identical with the first law, Eq. (33). The Eqs. (44) are the momentum equations, and it is immediately seen that q^κ/c^2 is a momentum, since its time rate of increase is equal to the negative gradient of the pressure.

Ohm's Law

The general problem of thermoelectromagnetic phenomena is too complex for brief discussion, but it is of interest to indicate how these phenomena may be included in the present theory. Consider an ideal fluid whose internal energy is independent of the electromagnetic quantities, but which is an electric conductor. A molten metal approximates such a fluid, but shows thermoelectric effects, etc., which indicate a slight dependence of its internal energy on the electromagnetic variables.

Let j^α be the electric current density in e.m.u./cm² sec. = e.s.u./cm³, and

$$F^{\alpha\beta} = \begin{matrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & -B_z & B_y \\ E_y & B_z & 0 & -B_x \\ E_z & -B_y & B_x & 0 \end{matrix} \quad (45)$$

be the field tensor, the E's being the electric field in e.s.u., the B's the magnetic induction in e.m.u. The energy-momentum principle is now to be formulated as

$$\partial W^{\alpha\beta}/\partial x^\alpha = j_\alpha F^{\alpha\beta}. \quad (46)$$

The tensor W can be resolved into components as before, and the first law becomes

$$-(\partial/\partial x^\alpha)(u_\beta W^{\alpha\beta}) + W^{\alpha\beta}(\partial u_\beta/\partial x^\alpha) = -j_\alpha u_\beta F^{\alpha\beta}. \quad (47)$$

This may be transformed into an equation similar to Eq. (33), except that the right side is not zero, but the same as that of Eq. (47).

The entropy and temperature may be introduced in exactly the same manner as above, and an equation, differing from Eq. (35) only by the additional term

$$-(1/\theta)j_\alpha u_\beta F^{\alpha\beta}$$

can be deduced. The Eq. (36) requires this term to be positive for all possible values of j_α and u_β; this will certainly be the case if (with $\sigma > 0$ and ρ a scalar)

$$j^\alpha = \rho u^\alpha - \sigma F^{\alpha\beta} u_\beta, \tag{48}$$

since $F^{\alpha\beta} u_\beta$ is a vector in proper-space. However, Eq. (48) is precisely the well-known invariant form of Ohm's law;[5] in the case of stationary matter it reduces to the classical form:

$$j^\alpha = \rho,\ \sigma E_x,\ \sigma E_y,\ \sigma E_z.$$

Thus ρ is the charge density and σ the electrical conductivity.

The ease with which this law can be incorporated into the equations lends strong support to the theory developed above. It will be noted that Maxwell's equations have not entered this discussion. However, the Eqs. (47) and (48) are too few to determine all the variables, and the Maxwell equations are needed to complete the theory.

[5] See Tolman, *Relativity, Thermodynamics and Cosmology*, p. 114.

Conclusion

It has been shown that the classical considerations of I can readily be extended so that they are consistent with the special theory of relativity. The further extension into the general theory should offer no special difficulties.

One result has appeared clearly: It is necessary to introduce the current-density of matter separately from the energy-momentum tensor. This is also apparent from other treatments of energy and matter, but has rarely been emphasized. From the macroscopic standpoint, therefore, matter cannot be considered a form of energy, even though inertia is a property of energy rather than of matter. Matter has inertia because it has energy, but is not a form of energy. This same conclusion can be reached from a consideration of recent attempts to construct microscopic theories of the ultimate particles.

Correction: The Thermodynamics of Irreversible Processes. II.

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On page 274 of the above paper, the sentence beginning "It is not easy to see . . ." should be replaced by the following:

It can be shown that

$$\textstyle\sum_i \Gamma_i(-\Delta_i/\theta) \geqslant 0$$

for all values of Δ_i. Let

$$x_s' = \textstyle\sum_k \nu_{ks}'\Delta_k/R\theta,$$
$$x_s'' = \textstyle\sum_k \nu_{ks}''\Delta_k/R\theta,$$

so that this sum may be written

$$R\textstyle\sum_s a_s[x_s' - x_s''][\exp(x_s') - \exp(x_s'')].$$

Since the exponentials are monotonically increasing positive functions of their arguments, it follows that both brackets in the above expression always have the same sign. Since $a_s \geqslant 0$, the required inequality follows at once.