Time's Arrow, Detail Balance, Onsager Reciprocity and Mechanical Reversibility: II. Thermodynamical Illustrations

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This concluding section applies the results of the previous part to some important thermodynamical systems. Even if time reversibility is allowed, it is shown that the flow vectors used to derive Onsager reciprocity from time translational invariance is of questionable validity. The fundamental fluctuation-dissipation theorem of Callen, Welton, Green and Kubo which underpin descriptions of irreversibility, insofar as they are derived from time-translational invariance, is also questioned; from Part I, they cannot be derived properly from time-reversal symmetry. The common view of entropy as some type of caloric fluid flow is critiqued as not conforming to the Kelvin-Clausius-Planck definition. An example of developing reciprocal relations to any order in the coupling indices based on the peculiar physical and defining characteristics of conductive heat is given for the steady state whenever a temperature gradient is present, free from time reversible and translation assumptions. A major challenge in the theory is to extend it to isothermal states. It is concluded that other more deterministic views mediated by authentic work anamnesis may be needed for long term coherence.

Keywords: time reversal, time translation, entropy production, irreversibility, Onsager reciprocity, fluctuation-dissipation theorems, isothermal and non-isothermal systems.

1. Introduction

This concluding part examines the restricted case of some thermodynamical systems of significance. It is demonstrated that most of the theories (such as the fluctuation-dissipation theorems of irreversible processes) cannot be derived from elementary non-contradictory axioms. The basic presuppositions and commonly accepted structures are first presented in Sec. 2 before alternative suggestions are provided in the latter portion of the work. Where reciprocity is concerned, it is shown that "conductive heat" is a pivotal physical concept, without which these relations cannot be developed within the present framework, thus underscoring the experimental and phenomenological aspect of the natural sciences. All too often, as shown in the text, the abstract formulation does not consider or take into account the rudimentary physics at all stages of a process, so one can legitimately question, following Einstein's criterion of a good theory in the celebrated EPR paper (Einstein *et al.* 1935, p.777) on whether or not these theories are reasonable in "explaining" phenomena. Clearly, abstract and often algebraic subsuming generalizations, sometimes written in haste, and which do not define the physical variables involved would all constitute incomplete theories if the Einstein criterion are admitted, since he states in the criterion: "*If, without in any way disturbing a* *system, we can predict with certainty (i.e., with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity*" where earlier in the paper, the necessary requirement of a complete theory is: "*every element of the physical reality must have a counterpart in the physical theory.*"

2. Comment on Onsager Thermodynamics, Entropy and Fluctuation-Dissipation Theorems

In his theory, Onsager (Onsager 1931a,b) only assumed the validity of microscopic (time) reversibility and detailed balance, without altering the general structure and meaning of the thermodynamical potentials and physical constants. Thus, within the structure of the potentials used which corresponds to physical observables, other theories which can account for the reciprocity behaviour may be considered as suitable alternatives to the Onsager description if detailed balance or microscopic reversibility is not to be assumed; an outline of how this might be partially achieved at the limit of steady states (in the same sense in which the Onsager theory was initially developed) and *non-isothermal systems* follows in Sec. 2.2 below, which has a modified entropy form compared to a previous development (Jesudason 1991a). Probably, some statistical axioms are required to extend the theory to isothermal systems, and appears as a significant challenge. It will be proven that even if the assumptions of microscopic reversibility and detail balance were assumed, the results that Onsager presented still appear to suffer from ambiguity stemming from the a_i stochastic thermodynamical displacement variables.

In the Onsager theory of Linear Irreversible Thermodynamics (LIT), the entropy deviation from equilibrium ΔS as a result of a displacement of thermodynamical variables a_i (where spontaneous fluctuations or direct perturbations cannot be distinguished from the regression hypothesis) may be represented as (Onsager 1931a,b, Reif 1965, pp. 36-41)

$$\Delta S = -\frac{1}{2}\sum_j \sum_j g_{ij} a_i a_j \tag{1}$$

The thermodynamical forces F_i are defined as

$$F_i = \frac{\partial \Delta S}{\partial a_i} = -\sum_j g_{ij} a_j \tag{2}$$

where

$$\langle a_i F_i \rangle = -k\delta_{ij} \tag{3}$$

and δ_{ij} is the Kronecker delta. The linear approximation gives

$$\dot{a}_i = \sum_j p_{ij} a_j \text{ or } \dot{a}_i = \sum_j L^*_{ij} F_j \tag{4}$$

where, $\dot{a}_i$ is actually a "fluctuational" derivative given by

$$\dot{a}_i = < a_i(t+\tau) - a_i(t) > / \tau \tag{5}$$

and where τ is larger than the relaxation time for molecular interactions τ_o, but smaller than the time of regression of a fluctuation τ_r, that is

$$\tau_o \ll \tau \ll \tau_r$$

The entropy production is given by

$$\dot{S} = \sum_i \dot{a}_i F_i \,. \tag{6}$$

Often $\dot{S}$ is equated with the internal entropy production (per unit volume) $\dot{\sigma}$ where "by the Second law", $\dot{S}$ ≥) and the total entropy differential dS' is allegedly given by

$$\mathrm{d}S' = \mathrm{d}_eS + \mathrm{d}_iS \qquad (7)$$

where d_eS is the supposed entropy brought in from the environment and d_iS is the differential entropy production inside a volume element (Prigogine 1961,p.16;Onsager 1931b, eqns (2.9-2.11)). A detailed analysis of the difficulties of this method of partitioning the entropy into "exterior and internal" terms with respect to thermostatic potentials has been discussed together with that of using Gibbsian-type potentials for non-equilibrium processes (Jesudason 1991a,b). If flows $\dot{a}$ are expressed in terms of (5), then the Onsager coordinates are defined to be properly chosen and reciprocity is assured where

$$\dot{\sigma} = \sum_i \dot{a}_i F_i = \sum_{ij} L^*_{ij} F_i F_j \geq 0 \qquad (8)$$

and $\dot{\sigma}$ is usually determined from Gibbsian thermostatic equations and a balance or continuity equation for entropy. It is essentially through such procedures, together with the postulate that $\dot{\sigma}$ ≥) that minimum entropy production theorems are derived (Prigogine 1961, p77; Yourgrau *et al.* 1982 p.14). A rationalization that might describe at least steady state processes is found in eqns. (1) and (6). Here, the coordinates are perpetually held at a distance from the equilibrium value, and the instantaneous relaxation values of the forces and fluxes (F_i and $\dot{a}$ respectively) at this coordinate point is taken to represent the values of the "entropy production" for the entire steady state as long as the coordinates (the a 's) are displaced a constant distance away from equilibrium. However, such a "constant" displacement would leave the entropy undefined because it is assumed that there is "entropy production" within a unit volume of the system whose temperature is fixed, whereas the thermal energy of a steady state system in any region is a constant, so that if the Kelvin-Clausius-Planck (KCP) definition of the entropy increment δS is considered, where $\delta S = \delta Q/T$, (δQ is the heat energy increment and T the Kelvin temperature) then there is in actuality no entropy production inside the volume sub-elements for fixed thermal energy since δQ vanishes on average (as will be elaborated). Despite this, the *ad hoc* use of thermostatic potentials allows for the presence of internal entropy production via the balance equation (Lavenda 1979, Chap.5-9). The analysis of non-equilibrium processes has imagined that entropy may be defined mathematically as a vector flow of thermal energy across a hypothetical boundary with a defined temperature (Honig 1982 pp. 396-400; Lavenda 1979 Chap. 5-9) where there might be local variation of temperature within the body. The KCP development of the Second Law precludes such considerations, where bodies are maintained at a fixed temperature, and thermal energy is introduced conductively and reversibly to a body via its diathermal boundary. It is claimed that these laws may be localized to exclude global system considerations. It has been shown that difficulties arise from such assumptions (Jesudason 1991a, 1991b).

The main argument of Onsager in deriving reciprocity conditions is that the dynamical laws of an isolated system are reversible (Onsager 1931a, p.411) in the sense discussed in the previous part (Jesudason 1999). Modern generalizations of Onsager's assumption refer directly to mechanics and its reversibility as well (Hurley *et al.* 1982).

However, problems arise even if we should suppose the above to be strictly allowed. Where no "Coriolis" forces act on the particle, reversing the velocities instantaneously would not cause a net change of the force vector on the particle. The thermodynamical variables a_i will then be even functions of the microscopic particle motions for each time parameter t for a particular defined equilibrium state undergoing spontaneous fluctuations; we may then take ensemble averages for each of the coordinates a_i, *i.e.* $<a_i(t)>$ for defined values of the other coordinates; the standard van Kampen

(1987) description of time reversal centered at time t, over the fluctuational differential τ must demand (Yourgrau *et al.* 1982, p.36)

$$\langle a_j(t+\tau)\rangle = \langle a_j(t-\tau)\rangle \tag{9}$$

i.e., there is an equivalent reverse motion for each forward motion. Now, since $<a_i(t)>$ is experimentally determinable, it implies that this quantity is a stochastic function of time t for a defined state and is a continuous function as the number of ensembles tend to infinity, *i.e.*

$$<a_i(t)> = \mathrm{A}_i(t) \tag{10}$$

As such, it does not necessarily follow that for any real δ,there is a time-translational invariance in the sense

$$\mathrm{A}_i(t+\delta) = \mathrm{A}_i(t). \tag{11}$$

From (9), it is conceivable, especially if the coordinates are not strongly coupled (so as to be independent variables) that

$$<a_i(t)\,a_j(t+\tau)> = <a_i(t)\,a_j(t-\tau)> \tag{12}$$

The important aspect of (12) is that the coupling of the right and left hand expressions via the specification of the appropriate time variable t, which is of the same value on both sides of the equation. From (3) and (4), we may derive

$$<a_j(t)\,a_i(t+\tau)> - <a_j(t)\,a_i(t)> = -\tau k L^*_{ij} \tag{13a}$$

and

$$<a_i(t)\,a_j(t+\tau)> - <a_i(t)\,a_j(t)> = -\tau k L^*_{ji}. \tag{13b}$$

In order to derive the reciprocity condition $L^*_{ij} = L^*_{ji}$ it is necessary to force the identity

$$<a_j(t)\,a_i(t+\tau)> = <a_i(t)\,a_j(t+\tau)> \tag{14}$$

in (13). This is achieved by supposing that it is permissible from “the postulates of statistical mechanics” to substitute $t+\tau$ for t on the right hand member of (12) whilst supposing that the left hand member need not be similarly substituted (Yourgrau *et al.* 1982, p.36) This argument raises several difficulties. The $<a_i(t)>$ are stochastic variables in time and may differ for each point in time since they measure the change of the variable during the regression of a fluctuation towards equilibrium and are therefore not time dependent for stochastic variables in “aged” systems. Thus the reason why the L^*_{ij}, when utilized in non-equilibrium studies is apparently “time-independent” appears little connected with the arguments of the equivalence of time or crowd averages (Prigogine 1961, p.51 eqn.4.45) which makes these coefficients “time independent” in the limit of infinite time, and which is experimentally corroborated, but is due to the fact that in the steady state, constraints (from the thermodynamic forces F_i) prevent the return of the system to equilibrium, and so “freezes” the coordinates at a particular point in time, where the rate of “entropy production” is that rate corresponding to the time t' when the system was regressing into equilibrium. The time coordinate t' is correlated to the magnitude of the forces (and consequently, “distance” of the thermodynamic coordinates from their equilibrium values). Thus, shifting times on one member of eqn. (14) implies a translation of the distance of the coordinate from equilibrium corresponding to a different value range of the thermodynamical forces, which contradicts the initial assumption. From what has been mentioned, it is therefore possible to map a coordinate (scalar) point t, with respect to a regression from equilibrium, such that (in the steady state)

$$\hat{\mathbf{T}}(\mathbf{F}) = \mathbf{t} \tag{15}$$

is a scalar product and **F** the thermodynamic force vector and $\hat{\mathbf{T}}$ an operator; a change of temperature alters the configuration of the system and the dynamics of fluctuations and hence the L^*_{ij} coefficients. We have made use of crowd or ensemble averages (not time averages) where for any time about t, (5) holds. If time averages are used, they cannot be extended over periods $|a| <<< \tau$ or else the notion of a "force" (defined in (2)) along a particular coordinate a_j is rendered meaningless, together with the velocity $\dot{a}_i$ of flux quantity j, since the derivative of the distance coordinate a_j with respect to τ yields the velocity within the regime of fluctuation. The study of the dynamics of the system is related to the regime where fluctuations occur; thus it is inappropriate to use time averages of a particular member of an ensemble to derive fluctuational (dynamical) averages; the time averages over infinity would yield values pertinent to the equilibrium properties of the system, not its "instantaneous" average value. Thus the justification given for supposing that no time dependence is implied in the Onsager theory is open to question, where time averages over a long time period is deemed valid to yield fluctuational average values (Prigogine 1961, p.51).

The immediate discussion above therefore appears to cast some doubt on the assumptions used to derive the fluctuation-dissipation theorem of Callen and Welton (also associated with Green and Kubo), according to the interpretation afforded by Brenig (1989) for the Callen-Welton formula

$$S_{kl}(-\omega) = S_{lk}(\omega)\, e^{-\beta\hbar\omega} \tag{16}$$

where the S_{kl} 's are defined according to a Fourier transform of the simple product correlation given by

$$S_{kl}(t) = <\Delta q_k(t)\Delta q_l(0)> = \frac{1}{\pi}\int_{-\infty}^{+\infty} S_{kl}(\omega)e^{-i\omega t}\,d\omega$$

where Δq_l is a coordinate of an observable of the system, and if equated with the same thermodynamical coordinates such as defined in (9-11) (*e.g.* $\Delta q_l \sim a_l$) above yields the time translational invariance identity

$$S_{kl}(-t) = S_{lk}\,(-i\hbar\beta) \tag{17}$$

On the other hand, Callen (1960) has commented on the importance of time reversal invariance in the derivation of his relations, which Brenig (1989) does not mention; in both cases, however, the present two-part work raises fundamental objections.

Where the "breakdown" of microscopic reversibility is concerned, it has hitherto not been attributed to the irreversibility of particle dynamics but to "hidden" variables, such that when other inversions (space, parity *etc.*) are considered, the overall system still exhibits an invariance (Lee 1988). A direct application of this "CPT" invariance theory to chemistry where "microscopic reversibility" is deemed to have broken down is in the treatment of enantiomeric mixtures subjected to physical agents such as electric and magnetic fields (Barron 1987). However, the train of thought here is not essentially dissimilar to Onsager's rationalization that when particles are subjected to "Lorentz forces" due to (magnetic) field intensity H, then the L coupling coefficients are even functions of the dynamical variables a, the modification for the coupling coefficient (Onsager 1931b, p.2279) is

$$L^{*}_{ij}(H) = L^{*}_{ji}(-H). \tag{18}$$

Casimer (Casimer 1945) merely generalized this result to include both Coriolis forces (of intensity α and the even or odd function nature of the L's under velocity reversal. One might say that this is an early example of "CPT" symmetry considerations (Lee 1988, pp.16-20)); the result being

$$L^{*}_{ij}(H,\alpha) = \varepsilon_i\, \varepsilon_j\, L^{*}_{ji}(-H,-\alpha) \tag{19}$$

where ε_i is +1 for a_i even in velocity reversal and –1 for a_i odd.

2.1 Some Consequences of the Above

The object of the above examples is to suggest that the ambiguity of the assumption of non-uniqueness of the motion relative to the time coordinate has lead to the treatment of both dynamical and static (equilibrium) phenomena in terms of non-deterministic theories (Gouyet 1996, pp.183-217), *i.e.* that which is not concerned with strict causality. Another possible supporting feature of this development is the influence of Heisenberg quantum theory, where non-commuting operators are interpreted to imply uncertainty in simultaneous measurement of the quantities signified by the operators; recently, it has been pointed out that this need not necessarily be the case (Jesudason 1998a).

I also suggest that the assumed apparent reversibility of Hamiltonian dynamics has spurred developments in the treatment of irreversible processes (Holian *et al.* 1987) from a fundamental statistical and mechanical point of view, where new equations are created to circumvent the assumed reversibility of Newtonian mechanics. Time reversal invariance of the Liouville equation has been invoked to extend the Boltzmann equation and entropy formulation (Kroner 1986). It is safe to conjecture that these new equations would not have been developed if it were not for the reversibility assumptions. The belief that thermodynamics (*e.g.* “entropy production”—including ‘internal’ entropy production, the meaning of which has been shown to be quite unclear) provides a ‘clue’ to the arrow of time which dynamics cannot provide has been a basis about which thermodynamical theorems have been created by Lavenda and others (Lavenda 1979,pp.105-106,108-109);curiously, on the other hand, aspects of microscopic reversibility have been employed in creating theorems on entropy (and power) production (Lavenda 1985, *e.g.* Chap. 1,pp.1-5 and pp.186-190) and equilibrium detail balance. The cosmological consequences of such reversibility assumptions in both the thermodynamic and dynamical sense is also evident in the works of astrophysicists (Hawking 1987).

From the above, it is clear that a concept of thermodynamical and statistical irreversibility based on some other criteria than mechanical reversibility can be constructed based on analytical determinism. The current trend seems to concentrate on acausal, often Universal-class prescriptions (as in fractal theory), which I believe is not without consequences in the sociology of science, such as the depersonalization of scientific work.

With regard to elementary (nuclear) particles, one might suppose that the time reversal introduced by such persons as E.P.Wigner, inspired by the developments of classical theories epitomized by the Boltzmann equation method which included microscopic reversibility (Delgado Domingos *et al. (eds)* 1974, p.81)) as an elementary fact in its initial development can only inspire the mathematical machinery of symmetry *via* group theory as a means of parametrizing the various species of nuclear particles and nuclear reaction processes as well as the geometry of all aspects of quantization. Such conceptions of symmetry have been thought to rigorously hold for the quantum thermodynamical and microscopic aspects of entropy (Delgado Domingos *et al. (eds)* 1974, p.98) as well. Considerations of symmetry and supersymmetry has not as yet lead to further unambiguous integrations of laws concerned with physical forces.

2.2 Example of Development of Reciprocal Relations

The partial example provided here of an alternative development of reciprocity without recourse to time-reversal invariance considers an entropy form which is free from the ambiguity of a previous definition, where reciprocity was also developed (Jesudason 1991a). In particular, this work results from both an appreciation and critique of the thermodynamic theories of Benofy and Quay (BQ) (Benofy *et al.* 1982; Jesudason 1989), especially in their conjecture of the nature of “conductive” heat and the Fourier law. The BQ development of the First Principle (an extension of the First law of thermostatics) has been experimentally verified (by Zamora and Rey de Luna) but unfortunately the analysis of their Second principle revealed inconsistencies, and a modified form (in the spirit of anamnesis) has been proposed and applied (Jesudason 1991a,b) to physical systems. The analysis of reciprocity is dependent on this modified form of the Second principle and the consideration of the thermodynamically irreversible Fourier heat conduction law, and the development of entropy according to the classical sense of Kelvin, Clausius and Planck (KCP) (Zemansky 1968) where the use of thermostatic potentials to derive flux quantities, such as the "entropy production" per unit volume of a steady state system displays inconsistencies (Jesudason 1991b). Previous work attempting to derive reciprocity outside of the above considerations has been found to be ambiguous (Edelen 1985, p360; Jesudason 1991a) and illustrates the subtle nature of non-equilibrium theory, including the importance of conductive heat (Jesudason 1989) in irreversibility and heat flow direction. Putative derivations (which all too often possess a spirit of haste and ambiguous, subsuming generality) have attempted to derive reciprocity without a physical basis (such as the unique direction of heat flow) by merely specifying a potential form, where reciprocity conditions obviously must be satisfied in Maxwellian potential theory irrespective of what the physical processes by virtue of the properties of an exact differential and the commutative nature of partial derivatives. The present theory assumes the existence of only one known temperature and heat exchange locally and a fundamental property of conductive heat. Furthermore, it is supposed that classical physical (CP) forms of energy also include heat exchange phenomena. Recently, a theory based on experimental observation has been developed to accommodate (small) *equilibrium temperature gradients* when the bodies at thermal equilibrium exchange energy *not* by Newtonian momentum conserving particles or quasi-particles (as Planck pointed out where electromagnetic radiation is concerned (Planck, 1959, p.55, Sec. 59-60)), as in the case of ordinary matter exchanging energy with photons (Jesudason 1998b). In such cases, the entropy increment dS must be modified to $dS = dQ/k'T$, where k' is a non-constant coupling function. In situations where the Zeroth law is valid, k' is a constant, and may be ignored, so that the entropy increment may be defined as $dS = dQ/T$. The example which follows assumes the validity of the Zeroth law, and is therefore of restricted application. No assumptions have been made with regard to nonequilibrium entropy being necessarily additive. The proper development of a field requires a combination of experimental investigations and theoretical rationalization (mediated strictly through a society which possesses absolute anamnesis of human effort). Therefore, work that claim to extend thermodynamics to the nonequilibrium regime without step-by-step experimental corroboration on mere analogy, deriving stability criteria, partial temperatures and heat increments, including the additivity of entropy and the use of thermostatic Gibbsian potentials and other quantities cannot be too helpful because the above mentioned structure of experimental corroboration and theoretical development through authentic human communion is practically non-prevalent (Delgado Domingos *et al. (eds)* 1974, p.9), leading to possible difficulties regarding definitions, terminology and interpretation, not to mention the possible breakdown in the continuity of thought which is required to address problems to future generations in a responsible manner. Also, some of these same developments presuppose adiabatic processes with attendant entropy increases (Delgado Domingos *et al. (eds)* 1974, p.9) whereas processes have been modeled on the basis of a "recoverable trajectory" with zero entropy increases (Jesudason 1991b) relative to the center-of-mass of the said trajectory and where there exists processes which are adiabatic and which conserves entropy for which Gibbsian-type potentials are inadequate to fully describe non-equilibrium states (Jesudason 1991b).

Temperature is in one sense a global (Jesudason 1991b) parameter of a system since a finite volume element is required for there to exist energy interchanges between oscillators and free particles so that in a steady state situation a temperature may be defined at any instant of time. Clearly, if averages are taken over time, then spatial extension is not a requirement, but the temperature cannot be specified accurately in a short span or instance of time. If a conductive fiber were placed at a point within this system, where even if the individual species concentrations within a region of the system does not have equilibrium distributions with respect to their statistical distribution (Fermi-Dirac, Bose-Einstein or mixed), the total energy interaction with the fiber will be distributed with an equilibrium distribution if and only if there is no net flow of thermal energy across the fiber which is connected at the other end to a thermal reservoir at temperature T, and where in this situation the non-equilibrium temperature of the region may be defined to be T also (Jesudason 1991a). The KCP statements of the Second law (Zemansky 1968,pp177-186) all refer to the global situation of the transfer of various amounts of energy called "heat" between the reservoirs and a thermodynamic system. There is a fixed temperature parameter within the entire volume which comprises the thermal reservoir by definition, and the entropy increment δS is defined as

$$\delta S = \delta Q / T = \frac{\int_{\partial C} \mathbf{J}_{\mathrm{q}} . \mathbf{dS} \mathrm{d}t}{T} \tag{20}$$

where dt is the increment of time, T the temperature, $\mathbf{J}_{\mathrm{q}}$ the conductive heat vector and $\mathbf{dS}$ the surface area increment of the reservoir. Conversely, the imputation of temperature *at an instant of time* requires spatial extension to accommodate system ensembles which interact with each other.

Changes in definition and meaning occur when other entropy forms, in an ad hoc way are introduced. By analogy with fluid dynamics *etc.*, "entropy" was envisaged as a fluid-like vector quantity (Callen 1946; Eu 1988 p. 68, eqn. 15; Onsager 1931a, p.421, eqn.5.7; Prigogine 1961, pp.19-20; Reichl 1980,Chap.4; Sorensen 1977, eqn 10) given as

$$\mathbf{J}_{\mathrm{s}} = \mathbf{J}_{\mathrm{q}}/T$$

where $\mathbf{J}_{\mathrm{q}}$ is a heat flow term. Then one can construct the quantity $\dot{\sigma}$ the rate of (internal) entropy production where the following balance equation is valid for all times (Callen 1946; Eu 1988)

$$\partial(\rho.\, s)/\, \partial t = -\nabla.\mathbf{J}_{\mathrm{s}} + \dot{\sigma} \tag{21}$$

where ρ is the density and s the specific entropy. [Concerning the Eu development (*op. cit.*), it has been shown from elementary calculus and the First Law that the Clausius inequality cannot exist (Jesudason 1993) for the trivial case of isothermal systems, invalidating for this instance at least the "compensated heat" derived from the supposed inequality used to construct a new entropy perfect differential for non-equilibrium systems.] A careful reading of Callen (1946) shows that he actually identifies $\dot{S}$ (the rate of entropy production) with $\dot{\sigma}$ at the steady state, which is precisely the Yourgrau position also (Yourgrau *et al.* 1982). From the above discussion, on the other hand, the requirement of spatial extension demands that at the steady state, the temperature distribution along any system must be represented by a three dimensional (Heavyside) step function, so that for a system with N volume elements each designated i, the entropy increase in the steady state can only be

$$\Delta S = \sum_{i}^{N} Q_i / T \tag{22}$$

where Q_i are the increments of heat absorbed from each of the elements i. Fourier heat conduction in metals where other cross effects are present such as the flow of electrons subjected to electric and magnetic fields have been treated by separating the different forms of heat flow (Callen 1946); where convective heat flow terms may be separable from the "lattice thermal conduction", although from the elementary theory of Linear Irreversible Thermodynamics (LIT) the material property coefficient is altered by cross-effects (Callen 1946). More complex LIT systems simply extend this separability of thermal energy flow to all the particle quantities concerned, so that heat conductivity has been defined by Callen (1946) as “the heat current density per unit temperature gradient for zero particle current”. This theme of net zero particle current is also developed in treatments of kinetic theory dealing with say Fourier heat conduction where the convective heat of transport is considered to be of a different effect from the conductive heat (Callen 1946, Chapman *et al.* 1970,pp.100,211 and 346) even in the steady state.

In what follows, this definition (which traces its origins in part to the use of thermostatic potentials for nonequilibrium situations) will be exchanged for another consonant with the entropy definition given in (22). It has been shown (Jesudason 1989) that the BQ effort to base a rigorous theory of irreversible (thermomagnetic) phenomena via the Fourier Inequality is not quite correct because the heat terms were misconstrued. However, it was pointed out that if the “conductive” part of the heat transfer is considered (in the Callen sense), then the Fourier Principle in relation to conductive heat flow is (unless proven otherwise) a general statement not immediately derivable from the Second law (though not violating it). In what follows, (Jesudason 1998b) we confine ourselves to systems which are comprised of particles or quasi-particles which exchange momentum according to Newton’s conservation law, or else a modification of the meaning of temperature and the Boltzmann coupling constant is required. A steady state situation is also assumed in the discussion.

We redefine the Fourier Principle as defining a process whereby

$$\mathbf{J_c}.\nabla T \leq 0 \tag{23}$$

is always true in any region of a system, where $\mathbf{J_c}$ is the conductive heat vector only, and in the absence of a temperature gradient, $\mathbf{J_c}$ is necessarily zero (Jesudason 1989).

Consider a volume element where δn particles of species n passes through in unit time with a characteristic thermal transport energy QH for the δn particles which occupy the volume element, having a non-equilibrium temperature T with respect to that whole volume element. We shall consider a new scheme for conserved flux quantities from the above modified Fourier Principle in the steady state only. Imagine that the species n moves through the lattice in the volume element in the steady state. The temperature may be determined by a diathermal fiber as outlined previously. This “stationary” lattice will be responsible for the conductive heat transfer with respect to that moving subsystem, immediately implying that the “lattice” can therefore be other subsystems also in relative motion with the subsystem of interest. Since the temperature profile of the volume elements are approximated by Heavyside step functions, each of the subsystems must give up its thermal transport energy at the boundary of the lattice, and this becomes part of the conductive heat term. There is also dissipative processes which convert work energy into thermal energy at the boundaries when the concerned subsystem of particles is acted on by a field which does work on the subsystem. In unit time, the amount of heat dissipated to the boundary of the subsystem is written as

$$\alpha.\,\delta\phi.\delta n \text{ where } 0 \leq \alpha \leq 1 \tag{24}$$

and where $\delta\phi$ is the change of potential energy of the field per unit number or mass of species n (depending on context, and where the other associated units are changed accordingly). The $(1-\alpha)\delta\phi.\delta n$ remaining units of energy is not dissipated as heat and may be utilized via a motor device to do work on the external environment (such as in a standard thermocouple circuit). The external heat flux for the next adjacent volume element must come from the lattice conductive heat, given as $\dot{Q}_{ext}(x)$, and so (we consider only a one dimensional situation which will be generalized) we write

$$\mathbf{J_c}(\mathrm{x}) = \dot{Q}_{\mathrm{ext}}(\mathrm{x}) \tag{25}$$

Our modified Fourier principle demands that the conductive heat at the other boundary end with coordinates x + δx and which is at a lower temperature than at point x must be the existing $\dot{Q}_{\text{ext}}$(x) plus the dissipation due to force field (work) dissipation and the change in thermal energy.

$$\begin{aligned}\mathbf{J_c}(x + dx) &= \dot{Q}_{\text{ext}}(x) + \alpha\delta(\phi\delta n) + dQH_n\delta n \\ &= \mathbf{J_c}(x) + .\alpha\delta\phi.\delta n + dQH_n\delta n \end{aligned} \tag{26}$$

since $\delta(\delta n)$ is zero for conserved quantities, and where δx is a unit distance and $\delta\phi$ is the change in potential over this distance; dQH_n is the thermal transport energy for species n.

In order to relate the present formulation with the experimental set-ups which has been configured to the Onsager theory, it is important to relate the so-called entropy production in the volume element, as opposed to that brought from the "outside", (Prigogine,1961) denoted by $\dot{\sigma}$ is given by eqn. (6) and

$$\begin{aligned}\dot{S} = \dot{\sigma} &= \sum_i \dot{a}F_i \\ &= \sum_i \sum_j L^*_{ij}\, F_i F_j \geq 0\end{aligned} \tag{27}$$

The KCP viewpoint as defined in this work cannot suppose that there is any such "internal" entropy production, since there is no net energy transfer to a system in a volume element, and that volume element is at a fixed temperature. We thus form the entropy increase in terms of the increase due to the thermal interchange across the boundaries of the sub-elements, so that

$$\begin{aligned}\nabla.(\mathbf{J_c}/T) &= \dot{S} = \dot{\sigma} \\ &= \nabla.\mathbf{J_c}/T - (\mathbf{J_c}/T^2).\nabla T \geq 0.\end{aligned} \tag{28}$$

From (26) and (28), and generalizing to three dimensions and N particle quantities due to the presence of species n_i (i = 1,2,...N) we derive

$$\dot{\sigma} = \sum_i^N \alpha_i \delta n_i \delta\phi_i / T + \sum_i^N dQH_i \delta n_i / T - \mathbf{J_c}.(\nabla T / T^2)\delta x \tag{29}$$

where δx is the unit positive distance, dQH_i the *thermal* energy change for species i, ϕ_i the change in force field potential per unit concentration.

From the postulated inequality $\mathbf{J_c}.\nabla T \leq 0$, it follows that

$$-\mathbf{J_c}.\nabla T/T^2 \geq 0 \tag{30}$$

Thus, from (28) and (29),

$$\sum_i (\alpha_i \delta\phi_i \delta n_i / T + dQH_i \delta n_i / T) \geq 0 \tag{31}$$

In many first order expressions (such as Ohm's law) n is positively proportional to ϕ, so that generally

$$\alpha.\delta n.\delta\phi/T \geq). \tag{32}$$

It can be shown that expressions (30) and (32) corresponds to the leading diagonal terms in the LIT expansions of the "entropy production" per unit volume *i.e.* $L^*_{jj}F_{jj}$. A major difference between the present work and LIT or other extensions thereof is that $\mathbf{J_c}$ is a composite term which is a function of the entire species flows and their energy interaction where a temperature is defined and thus applies directly to fluid thermodynamics also where a conventional "lattice" is deemed not to exist over a particular volume element, and is defined even when there is a net particle flux in a particular direction; the form $\mathbf{J_c}$ reduces to that of ordinary heat conduction (in solids) where there is no net particle flow.

No principle of "local equilibrium" in the sense that the Gibbsian equations of thermostatics is valid in non-equilibrium steady states is assumed in this scheme; only the Zeroth law as assumed for each particle flux in a unit volume so that a single unique temperature characterizes each individual species distribution with respect to all other species in the volume element. This is a generalization of the assumption in the original development of the Brownian motion theory which considered the independent collective behavior of solute molecules in a solvent matrix which was maintained at constant temperature (Einstein 1956, p.8-18, 77).

The complete set of independent variables for QH_i is denoted by the vector function **v**, and it may of course include such variables as the potentials ϕ_i.

We define the thermodynamical force F_i as

$$F_i = (1/T)\partial QH_i/\partial \mathbf{v}.\delta\mathbf{v} \tag{33}$$

In (unit) time δt, we may express (29) by expanding dQH_i as in (33) to yield

$$\delta S = -(\mathbf{J}_c.\nabla T/T^2)\delta t + \sum_i \alpha_i \delta\phi_i \delta n_i / T + \sum_i \delta n_i F_i . \tag{34}$$

In LIT, a fundamental assumption is that the fluxes δn_i are a linear function (Onsager 1931b, eqn.1.11) of the forces F_i, where in fact we make a more general assumption by writing

$$\delta n_i = \delta n_i(F_1, F_2 .... F_N) \text{ where } n_I(0) = 0, \tag{35}$$

so that to first order, we may write in unit time

$$\delta n_i = \sum_z^N L_{iz} F_z \qquad where \qquad L_{iz} = \partial \delta n_i / \partial F_z \,|_{F=0} . \tag{36}$$

It has been demonstrated that $\delta n_I\, dQH_I/T$ is a perfect differential (Jesudason 1991a)) where the factor δn_i is derived from the fact that the present subsystem is not a fixed number of particles that traverses a circuit, but a portion of it which is contained in a fixed volume region common to all other flow quantities in that region.

Since $\delta n_i dQH_i/T$ is a perfect differential, then so must $\delta S'$, given by

$$\delta S' = \sum_i^N \delta n_i F_i \tag{37}$$

so that the (Maxwellian) perfect differential criterion yields

$$\frac{\partial \delta n_i}{\partial F_j} = \frac{\partial \delta n_j}{\partial F_i} \tag{38}$$

where within the LIT framework (36) gives

$$L_{iz} = L_{zi}. \tag{39}$$

This condition is only approximate. Eqn. (36) states that the forces F_j are to be considered "independent" and so we might expand to second order for greater accuracy to yield

$$\delta n_i = \sum_z L_{iz} F_z + \sum_j \sum_k K_{ijk} F_j F_k \tag{40}$$

where from the Taylor expansion, we identify

$$K_{ijk} = \frac{1}{2} \frac{\partial^2 \delta n_i}{\partial F_j \partial F_k} \Big|_{x=0}$$

and assuming convergence of the expansion and from the commutative property of partial differentials

$$K_{ijk} = K_{ikj}.$$

The reciprocity conditions (40) yields

$$L_{ip} + 2\sum_z K_{ipz}F_z = L_{pi} + 2\sum_z K_{piz}F_z \tag{41}$$

If in (41) we allow $L_{i_p} = L_{p^i}$, then (41) is equivalent to

$$\sum_z (K_{ipz} - K_{piz})F_z = 0 \tag{42}$$

Since F_z is "independent" and arbitrary from the LIT approximation, (42) gives

$$K_{ipz} = K_{piz.}$$

If L_{pi} is symmetric, then so is $K_{i_{pz}}$ in its indices. Using a proof by induction, it follows that the K coefficient is symmetric in its indices to all orders (or to all ranks). Other properties may be deduced from topological and differential form considerations.

For systems subjected to for instance a magnetic field which might induce changes in the velocities of the flow due to the opposing forces if reversed, approximations must be made with regard to the nature of the interactions before one can make first order Casimer deductions as to the form the reciprocal relations might take.

It is not possible to derive these relations from purely mathematical manipulations, interpolations and subsuming, and without making clear assumptions regarding the physical basis of the system behavior. The mathematics will always have an aspect of potential theory, but cannot in itself express the experimental aspects of reciprocity (Edelen 1985). We have resorted to a modified conjecture regarding conductive heat to derive the above, preserving the particular anamnesis of Benofy and Quay. One unresolved question here is to derive the reciprocity condition for isothermal systems (where the temperature gradient is absent and where the modified Benofy and Quay conjecture does not obtain). This appears to be a major challenge.

3. Conclusion

From probability theory and mechanics in the previous part, and from the various correlation function analysis of this sequel, it has been shown that detailed balance has been understood and applied more in an *assumed sense* - since it does not derive directly from mechanics- to fundamental processes such as those described in the fluctuation-dissipation theorem (Agarwal 1973; Callen 1960,p.284; Case 1972, eqn.74; Cassuto *et al.* 1981, eqns. 8,10,11 & 12; Davies 1977, pp.56-59,70-74,180-185; Green *et al.* 1951, Hurley *et al.* 1982, paragraph above eqn.1; Keizer 1976a, p.1679, eqn.14; 1976b, p.4467 Sec. IIIA, p.4469 eqn. 16; 1985, p.2751 Sec.I; King 1978, Sec V(C); Kubo 1957; Majewski 1984; Sachs 1987, esp. Chaps 1-2) including early use of CPT theories to characterize nuclear processes (Lee 1988).

Preliminary and rudimentary attempts have been made to derive kinetic equations without recourse to reversibility concepts (Jesudason 1991b), where a general characteristic time parameter τ which describes a class of processes, such as Fourier Heat Conduction that are entropy invariant with respect to a center of mass (energy) frame emerges, but as yet, a detailed, purely mechanical derivation of entropy which is able to also predict the direction of evolution of the system has not yet—as far as I am aware—been developed. Such a development along deterministic lines would employ a generation of workers each endowed with unique and complimentary gifts together with an open media that is capable of maintaining extensive citation and work anamnesis of persons. Hopefully, the complementary nature of thermodynamics as a study of the continuous and discrete (and currently statistical), without the one being considered 'more fundamental' than the other would be appreciated, because the macroscopic aspects determine the boundary conditions for the solution of the statistical model. Certainly it might be worth while examining the classical origins of this concept, such as is found for instance in the Clausius-Boltzmann (Roldughin 1984) Stosszahlansatz before considering quantum analogues.

From the above, it is clear that a concept of thermodynamical and statistical irreversibility based on some other criteria than mechanical reversibility can be constructed based on analytical determinism.

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