

Time's Arrow, Detail Balance, Onsager Reciprocity and Mechanical Reversibility: I. Basic Considerations

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This first part analyses the mechanical and statistical basis of time reversibility concepts which have played a pivotal role in constructing fundamental theories in irreversible thermodynamics and quantum physics. It is concluded that these concepts cannot be derived from classical mechanics and statistics, but seem to be more like axioms, which claim to have foundations in classical mechanics and statistics. The sequel will attempt to suggest how alternative formulations might be developed.

Keywords: detail balance, reciprocity, CPT symmetry, time reversal, entropy, irreversibility

Preface

Whilst preparing for the 92nd AAAS conference in San Diego, U.S.A. (2011), the author noticed that this particular work had not been typeset properly according to the galley proof corrections, where the equation references in the text were often incorrect. I am grateful that Roy Keys has agreed to re-publishing the corrected version after a time lapse of about 12 years. The modern theories of Physics have incorporated ideas of mechanical reversibility and CPT invariance in quantum mechanics and particle theory. The current work shows that these time honoured formulations are mathematically questionable despite their large scale and coordinated utilization.

The manuscript remains largely unchanged and any modification to the original text is denoted by words within square [..] parenthesis.

Introduction

The concepts of time reversibility, detail balance, system evolution and entropy are closely connected, where time reversibility assumptions stem from considerations in mechanics, whilst all the latter phenomena are often described as a marriage of mechanics with statistical theories.

In order to determine the limits of validity of the core assumptions used in describing the above, one must examine master equations and kinetic processes, because the master equations used to model kinetic processes often involve factors called the transition probabilities (Thomsen 1953) which are constructed to sometimes exhibit properties of time reversal symmetry. The principle of microscopic reversibility, which features strongly in Onsager thermodynamics (Onsager 1931a,b) and other aspects of physical theory (Whittle 1986) states that (to first order) the transition probabilities linking any two different states are identical for that ordered pair of states (Thomsen 1953, Sec

II). Since these transition probabilities are sometimes assumed invariant in regimes away from thermostatic equilibrium they provide a link in relating the thermostatic probability density of states and their kinetic coefficients to those away from equilibrium which are also solutions of the Fokker-Planck equation. This standard technique is widely utilised (Agarwal 1973; Case 1972, eqn.74) especially in "fluctuation-dissipation" theories that derive kinetic coefficients from equilibrium densities.

The analysis of the validity of these concepts is dependent in turn on mechanics and probability theory which we shall consider first in the following section. We observe that most workers in irreversible thermodynamics are not concerned (Zak 1996) with the limits of validity of the assumptions, which are taken as axiomatic, but on elaboration about these axioms. This does not necessarily imply that the current work would jeopardize their detail formulations; at most it might modify interpretation. Similarly, others, (Karakostas 1996) concentrating on other more philosophical aspects, have provided a *metacritique* of some aspects of the arrow of time without focussing on these assumptions such as the reversibility in time of the Hamiltonian or wavefunction. Our primary objective, on the other hand, is to analyse the axiomatics, with the intention of encouraging efforts aimed at descriptions of nature that is more mechanical and deterministic, with minimal assumptions concerning the microscopic laws obeyed by the system, so as to moderate the tendency in current developments which emphasizes both non-locality and non-determinism (due perhaps to the influence of quantum mechanics), notably in the fractal treatment of thermodynamics and chaos, where Universality of critical exponents for instance are postulated without strict mechanical (causal) deduction (Gouyet 1996).

1. Classical Mechanical Considerations

There are two basic mechanical principles, (Tolman 1950, p.102) namely the principles of dynamical reversibility and reflectability which underpin current descriptions of irreversibility, and in thermodynamics, the development of the entropy formalism contained in the Boltzmann H -Theorem (Keizer 1976a, paragraph about eqn.14)) and various fluctuation-dissipation theorems attributed to Callen and co-workers (Delgado Domingos *et al.* (eds) 1974, p.173)) and their quantum analogues. Thus, the limits of validity of these principles is important for deciding on a basis to describe thermodynamic irreversibility, and this point will be considered after examining the principles.

1.1. Reversibility Principles

The principle of dynamical reversibility states (Tolman 1950, p.102) (by suitable choice of initial conditions) that for conservative Lagrangians or Hamiltonians symmetric in their momenta there exist two solutions to the equations of motion, $(-t, q, -p)$ and (t, q, p) where $t, q,$ and p are the time, position and momentum co-ordinates respectively, whilst the principle of dynamical reflectability states (in Euclidean space, Cartesian co-ordinates) that for positive time, there exists independent solutions (x, y, z) and $(x, y, -z)$ for a system co-ordinate. These principles obtain for strictly mechanical systems. The importance of these statements for many particle thermodynamics is that for steady state conditions where there is a net particle flux, there exists an average potential due to the structure of the system $V(x_i)$ for particle flux species x_i , and thus the above principles are applicable to the average motion of particles, which yields the detail-balance condition (Onsager 1931a,b; Yourgrau *et al.* 1982, p. 35-39) which some consider more fundamental than the Second law (Thomsen 1953), a force-field $-\nabla V(x_i)$ and symmetry conditions in the case of dynamic reflectability. The considerations below are for a Euclidean space (Cartesian co-ordinates) system of particles with unit mass.

equated to $s'(-v'_1, -v'_2 \rightarrow -v_1, -v_2)$ representing line B'A', violating the specified vector direction of the transformation.

1.3. Principal of dynamical reflectability

It follows from the above that for the stated form of the Hamiltonian, two distinct solutions do not exist in positive time. It is also possible to make this conclusion from the proof of this principle, as given by the treatises (Tolman 1959). For Lagrangian systems with the above stipulated conditions (including the potential V being an eigenfunction of the co-ordinates), the proof of the principal is to compare the Euler-Lagrange (EL) equations for a particle trajectory for all three co-ordinates (set 1) with another (set 2) with the same form except that the $i = 3$ co-ordinate replaced by another reflected set:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}_i} \right) - \frac{\partial L}{\partial x_i} = 0 \quad \{i = 1-3\} \text{ (set 1)}$$

$$\frac{d}{dt} \left[\frac{\partial L}{\partial (-\dot{x}_3)} - \frac{\partial L}{\partial (-x_3)} \right] = 0 \quad \text{(set 2)}$$

Then if $\{x_i = g_i(t), i = 1,2,3\}$ is a solution for set 1 then it is maintained that $\{x_i = g_i(t), i = 1,2, x_3 = -g_3(t)\}$ (Tolman 1950, pp. 100-101) must also be a solution. However, for Lagrangians symmetrical in the velocity variables, the $i = 3$ (set 2) equation is equivalent by multiplication by -1 to the $i = 3$ (set 1) equation so that a distinct solution is not anticipated. The importance of this principle is that it envisages a plane of reflection, so that for a specified motion, (Tolman 1950, p.102) "*any motion of a system and any mirror image or enantiomorph of that motion would be equally possible.*" Thus, violations in handedness would be said to exist when experiments do not show equal proportion of measured intensities of properties arising from enantiomorphic motion. Furthermore, such a development justifies Onsager setting the equality to the following correlation function (Delgado Domingos *et al.* (eds) 1974, p.76)

$$\langle x_1(0)x_2(t) \rangle = \langle x_1(0)x_2(-t) \rangle \quad (1)$$

when usually, however, other statistical developments demand transforms which negate the momentum and time to preserve time reversibility.

If the forces are specified for the particle motion at each infinitesimal segment of the true path, then for the k th particle, the co-ordinate \mathbf{r}_k is

$$\mathbf{r}_k = \int^t \int^{t'} \mathbf{F}_k(t'') dt'' dt' \quad (2)$$

so that two arbitrary constants (*e.g.* the position and velocity) is sufficient to uniquely define the path. Since \mathbf{F}_k does not change sign upon reversing the motion [momentum] in negative time, there can be only one unique path in positive time (to two arbitrary constants) which contradicts the standard assumptions (Yourgrau *et al.* 1982, p.81). The quantum analogues of detailed balance follow a similar form of reasoning as is found in classical derivations and may be similarly examined.

The extension to quantum mechanics is currently dependent on the validity of 'microscopic reversibility' in the sense that Newton's laws or Hamiltonian dynamics do not imply irreversibility, and this type of conviction appears to be the basis on which E.P. Wigner, Schwinger and others developed a theory of time reversal in quantum mechanics (Sakurai 1964 Chap. 4; Wigner 1959 Chap. 26) and applied them to physical systems, such as in particle physics and those attributed to degenerate levels (Kramer's degeneracy) in atomic spectra (Wigner 1959, Chap. 26; Kpupicka *et al.*

1968, pp. 166,193-196). If it were true that Newton's laws of motion were "reversible" in this commonly assumed sense (Sakurai 1964) then the Onsager 'principle' that both directions of a thermodynamic path are traversed with equal frequency (microscopic reversibility hypothesis) in any physical system would seem a most reasonable assumption in equilibrium at least, because of the "neutrality" in the direction of motion given a fixed force field configuration. Since this is not generally the case, then the current thermodynamical developments in at least the Callen, Onsager and Prigogine sense (Glansdorff *et al.* 1954; Pathria 1977) may be opened to question.

Wigner time reversal in quantum mechanics is achieved by supposing that the diagonal elements of Hermitian operators have classical analogues, that is, that the expectation values of certain quantum mechanical operators such as for momentum and position corresponds to the classical behavior of systems within the appropriate limits. For instance, under the time reversal operator, \hat{T} , the following are assumed to result for the expectation values of a quantum mechanical system, *i.e.*

$$\hat{T} x \hat{T}^{-1} = x, \hat{T} p \hat{T}^{-1} = -p, \hat{T} L \hat{T}^{-1} = -L, \text{ and } \hat{T} t \hat{T}^{-1} = -t \quad (3)$$

where x , p , L and t represent the position, momentum, angular momentum and time co-ordinates respectively (Sakurai 1964 p.82). These quantities would yield new properties as a result of 'time reversal' if descriptions such as van Kampen's are assumed (Williams 1971, p.103-108); from the preceding arguments, on the other hand, if new properties do result from such operations, they must be due to intrinsic system symmetries of the Hamiltonian that allow for these operations to determine the new properties, and not to the general algebraic properties assumed for the Hamiltonian in time reversible assumptions. For instance under time reversal, the wave equation for the free particle is represented by a particle physically traversing (in positive real time) in the opposite direction to the particle when not under time reversal (Sakurai 1964 p.83, eqn.4.22). The technique used to derive further equations from time reversal is to relate the properties of the classical Poisson brackets to the quantum mechanical commutation relationships (Sakurai 1964, pp. 82,86). The Poisson brackets in classical mechanics actually provides the conceptual link to the quantum mechanical commutation relationships (Leech 1958, pp. 90-94). Recently, it has been proposed that the quantum-mechanical commutation relations reflect global and not local properties, and thus one may question the application of local transformations to global properties (Jesudason 1998a).

The influence of these "principles of time reversal invariance" has been deep and far reaching in particle theory where it constitutes the fundamental means of analysing nuclear processes (and in thermodynamics, at least in the Callen, Kubo, Onsager and Prigogine sense). In particle physics, the ideas of "symmetry violations" are based on such ideas as space and time invariances and reversals (Lee 1988 pp. 16-20). We would like to propose that such a type of assumed procedure with regard to classical time reversal (and possibly other) invariances have led to an interpretation of nature where symmetry and symmetry violations have become the basis for postulating theorems in particle physics, technically known as CPT symmetry principles (Lee 1988 p.16) and in irreversible thermodynamics. Perhaps the "element of surprise" which accompanied the results of the decay of Co^{60} was in part conditioned by the inherent belief in the symmetry properties of the Hamiltonian, including its "time reversed" properties (Lee 1988 p.4) as outlined in the Tolman postulates. The incorporation of "time reversal" adds yet another mathematical property to the resulting equations, where the transformation of the Hermitian operators under say parity has a form not dissimilar to those for time reversal (Sakurai 1964, p.81 eqns 4.7-4.10). This would introduce all kinds of properties which may be correlated and contrasted to experimental results, leading to the apparent violations *etc.* In quantum theory, time reversal ideas have been applied to the commutation relations between co-

ordinates and momentum (Brenig 1989, p. 39) to keep them invariant with respect to time reversal, and one has to choose the time reversal operator as an antilinear operator $\tau a = a^* \tau$, where a is an arbitrary complex number, where τ is defined as follows:

$$Tq_k(t)\tau^{-1} = q_k(-t) = \sigma_k q_k = \begin{cases} +1 \\ -1 \end{cases} \cdot q_k \quad \text{for} \begin{cases} \text{coordinate-like} \\ \text{momentum-like} \end{cases} \text{ operators} \quad (4)$$

Recently (Jesudason 1998a), it has been proved that for instances of the same domain space for the co-ordinates and momenta, the commutation relations such as $[\hat{p}_k, \hat{q}_k] = i\hbar f(\hat{q}_k)$ can only be true in a global sense, and so the antilinearity of τ would have to be interpreted in a similar vein to circumvent contradictions. [More precisely, it was shown that $[\hat{p}_k, \hat{q}_k] = 0$ for the same domain space, so that $[\hat{p}_k, \hat{q}_k] = i\hbar f(\hat{q}_k)$ is true only in the global sense and may not pertain to local coordinates in the same domain space.]

2. Gibbs ensemble and statistical considerations

2.1. Results from probability theory and the Gibbs' Ensemble

We use the standard notation of set theory in our equations (Rozanov 1977, Chaps 2-3) We note that events separated in time by the time parameter t in any one frame of reference may be viewed as constituting separate classes of these same events at different times, where these events form non-empty set classes denoted by $A_1, A_2, \dots, A_n; B_1, B_2, \dots, B_n$, and so on in the time domain of mutually exclusive events. This argument is strictly classical in its viewpoint where any event is recognised without having temporal extension, that is, it occurs at a definite time within any one frame of reference. Special relativity apparently does not address this issue and neither does any extensions thereof. Thus, we write for the probability of event A occurring at time t denoted by $P[A(t)]$ the following expression

$$\begin{aligned} P[A(t)] &= \sum_k P(A | B_k(t - \delta t)) \cdot P[B_k(t - \delta t)] \\ &= \sum_k P[A(t)] P[B_k(t - \delta t)]. \end{aligned} \quad (5)$$

Here, the events B_1, B_2, \dots, B_n precede event A and they form a complete set of events from which event A may arise after time δt .

Suppose we prepare N identical systems at time $t' = 0$ and examine them at time t . Let the number of systems with quantum numbers r and q (where r and q may represent a vector of quantum numbers) at time t be denoted by $\epsilon_{r,q}$. Then, relative to the initial state, we define the probability (if it exists) of the state $\chi(r,q)$ at time t as

$$P_{r,q}(t) = \lim_{\epsilon, N \rightarrow \infty} (\epsilon_{r,q} / N). \quad (6)$$

If only one system were prepared and we determine after time t the state of that system (having the same initial state as the above ensemble) and repeat the procedure N' times, then we may define the probability of the system to be in the state $\chi(r,q)$ at time t as

$$P'_{r,q}(t) = \lim_{\epsilon', N' \rightarrow \infty} (\epsilon'_{r,q} / N') \quad (7)$$

where $\epsilon'_{r,q}$ is the number of times the system is in state $\chi(r,q)$ after time t within the set of N' measurements. A common postulate of statistical mechanics asserts (the Ergodic theorem) that for distinguishable systems

$$P_{r,q}(t) = P_{r,q}(t). \quad (8)$$

We shall suppose for simplicity (suitable generalisations are possible but shall not be considered here; by and large it is anticipated that the final results will not differ significantly from this simplified treatment) that the systems are (α) distinguishable and (β) conserved (*i.e.* the system cannot split into two or more systems) when ensemble averages are taken. We may then represent each system as one unique line trajectory in time, puncturing a particular quantum mechanical set of states at any time t where the set of states may be represented as a convenient system of co-ordinates in geometrical space. Interference and correlation phenomena (as in the electron diffraction double slit experiments) may in some instances not allow measurements to be made on a particular system of the ensemble which will not also affect the trajectory of other systems. If these effects were not present, then it would be possible to continuously monitor the state of the system over time, *i.e.*, the values of their state variables if there is no interference between the measuring device and the particular member of the ensemble. If correlation effects between systems are significant, then we may describe the average trajectory of a system by determining the value of the state variables at any time t_m and then bring back the system and the ensemble to the initial state and measure the state variables again at the same time interval t_m . The average value of the state variables for any time t_m may be determined by repeating the above procedure until an average limit is reached as the number of times the procedure is repeated increases. This method of determining the average trajectory may be employed if there is cross interference effects between the measuring device and the ensemble member even if there does not exist significant correlation effects between systems in the ensemble. The term $\varepsilon_{r,s}$ represents the number of trajectory lines that puncture the region that belongs to the state $\chi(r,s)$. In what follows, we assume that the appropriate limits have been taken (the ε 's and N 's all tend to infinity).

The change in the probability $\delta P_{r,s}$ of the system being in the state $\chi(r,s)$ between time t and $t + \delta t$ is then given by

$$\begin{aligned} \delta P_{r,s} &= \Delta \varepsilon_{r,s} / N \\ &= - \left(\frac{1}{N} \right) \{ \varepsilon_{r,s}(t) - \varepsilon_{r,s}(t + \delta t) \} \end{aligned} \quad (9)$$

From Eqns. (5), (6), (7) and (9) we write the transition probabilities λ as

$$\begin{aligned} \lambda_{rs,qz}(t) &= \varepsilon_{r,s}^{q,z}(t) / \varepsilon_{r,s}(t) \\ &= P_{r,s}^{q,z}(t) / P_{r,s}(t) \end{aligned} \quad (10)$$

where for instance

$$P_{r,s}^{q,z} = \lim_{N \rightarrow \infty} \lim_{\varepsilon_{r,s}^{q,z} \rightarrow \infty} \varepsilon_{r,s}^{q,z} / N \quad (11)$$

and where $\varepsilon_{\alpha,\beta}^{\phi,\xi}$ represents the number of system trajectories which puncture the state set $\chi(\alpha,\beta)$ at time t and end up finally in the quantum state $\chi(\phi,\xi)$ in the further (unit) time δt . The subscripted variables represent the initial trajectory class and superscripts the final trajectory destination for any time interval. For what follows, the λ transition probabilities and ε 's are all functions of time unless otherwise indicated.

From (9), the total number of trajectory lines puncturing the state $\chi(r,s)$ at time $t + \delta t$, $\varepsilon_{r,s}(t + \delta t)$ must be given by:

$$\varepsilon_{r,s}(t + \delta t) = \sum_{\alpha} \sum_{\beta} \varepsilon_{\alpha,\beta}^{r,s}(t) \quad (12)$$

where

$$\Delta \varepsilon_{r,s} / N = -\varepsilon_{r,s} / N + \left(\sum_{\alpha} \sum_{\beta} \varepsilon_{\alpha,\beta}^{r,s} \right) / N \quad (13)$$

From [(9)], (10) and (13) we derive

$$\delta P_{r,s} = -P_{r,s}(t) + \sum_{\alpha} \sum_{\beta} \lambda_{\alpha\beta,rs} \cdot \varepsilon_{\alpha,\beta}(t) / N \quad (14)$$

From (10) and (12), the conservation of the number of systems and the definition for the ε 's, we have

$$\begin{aligned} P_{r,s}(t) &= \sum_q \sum_z \varepsilon_{r,s}^{q,z} / N \\ &= (\varepsilon_{r,s}(t) / N) \cdot \sum_q \sum_z \lambda_{rs,qz} \end{aligned} \quad (15)$$

Thus, from (14) and (15)

$$\delta P_{r,s} = -P_{r,s}(t) \sum_q \sum_z \lambda_{rs,qz} + \sum_{\alpha} \sum_{\beta} \lambda_{\alpha\beta,rs} P_{\alpha,\beta}(t) \quad (16)$$

which is similar to the standard thermodynamical expression (Cox 1950, eqns.(1-2)) for the master equation

$$\dot{P}_i = \sum_j (P_j - P_i) \lambda_{ij} \quad \text{or} \quad \delta P_i = \left(\sum_j (P_j - P_i) \lambda_{ij} \right) \delta t \quad (17)$$

2.2 Transitions in coupled systems

Having defined the terms involved in the standard representation (Cox 1950), we now consider the case of coupled transitions, such as that of a system in state i coupled to a heat bath (reservoir or some other system) with quantum state p ; let there be a transition of the system to state j , and the heat bath to state r . The transition probability is given (in unit time) by $\lambda_{ip,jr}$.

The total transition per unit time from state i to state j of the system (for all values of p and r) is given by λ_{ij} . Now, according to the standard representation of the master equations (Cox 1950, p.242) the following relations hold:

$$\lambda_{ij} = \sum_r \sum_s P_r' \lambda_{ir,js} \quad (18a)$$

where

$$\begin{aligned} \lambda_{ji} &= \sum_r \sum_s P_s' \lambda_{js,ir} \\ &= \sum_r \sum_s P_s' \lambda_{ir,js} \quad (\neq \lambda_{ij}) \end{aligned} \quad (18b)$$

$$\dot{P}_i = \sum_j \lambda_{ji} P_j - P_i \lambda_{ij}$$

and

$$\lambda_{ir,js} = \lambda_{js,ir}$$

where the primed quantities refer to the reservoir states.

If the system and the reservoir together constitute an isolated system, then all transitions for this combined system must be energy conserving. Then for any actual transition $ir' \rightarrow jp'$, the conservation of energy implies the existence of some function F whereby $F(i,r') = F(j,p')$ for all transitions that conserve the total energy of the system.

The equations written previously for the generalized Gibbs ensemble is directly applicable to this system, provided that the functions are so defined that there is no violation of the principle of

conservation of energy. The state of the combined system is given by $\chi(i,r)$ where it is supposed that if the interaction Hamiltonian between the system and the reservoir is very small in absolute energy, then the state of the system is given by the quantum state i of the system and the quantum state r of the reservoir (usually a product state ij). The probability of the system being in state j , denoted P_j is defined as

$$P_j(t) = \frac{\left(\sum_s \mathcal{E}_{j,s}(t) \right)}{N} \quad (19)$$

where

$$\mathcal{E}_j(t + \delta t) = \sum_q \sum_p \sum_r \mathcal{E}_{q,p}^{j,r}$$

with

$$\mathcal{E}_{q,p}^{j,r} = 0$$

if there is a violation of the law of conservation of energy.

From (10) the transition probability from system state j to i in (unit) time δt may be written

$$\lambda_{ji} = \frac{\sum_p \sum_x \mathcal{E}_{j,p}^{i,x}}{\sum_s \mathcal{E}_{j,s}(t)}$$

or

$$\lambda_{ij} = \frac{\sum_p \sum_x \mathcal{E}_{i,p}^{j,x}}{\sum_s \mathcal{E}_{i,s}(t)} \quad (20)$$

where

$$\sum_i \sum_s \mathcal{E}_{i,s}(t) = N$$

and

$$\sum_i \sum_p \sum_j \sum_x \mathcal{E}_{i,p}^{j,x} = N.$$

Define W'_{ij} such that

$$W'_{ij} = \left(\sum_p \sum_x \mathcal{E}_{i,p}^{j,x} \right) / N. \quad (21)$$

Then from (18b) and (20) $W'_{ij} = \lambda_{ij} P_i(t)$ so that the total change in the probability of state j in unit time $\delta P_j(t)$ is given by

$$\begin{aligned} \delta P_j(t) &= -\sum_i (W'_{ji} - W'_{ij}) \\ &= \sum_i (P_i \lambda_{ij} - P_j \lambda_{ji}) \end{aligned} \quad (22)$$

which is also the master equation given by standard treatments in eqns (18).

However,

$$\lambda_{rs,qz} = \frac{\mathcal{E}_{r,s}^{q,z}}{\mathcal{E}_{r,s}} \quad (23)$$

where

$$\epsilon_{r,s} = \sum_{\alpha} \sum_{\beta} \epsilon_{r,s}^{\alpha,\beta}.$$

Hence if

$$\lambda_{rs,qz} = \lambda_{qz,rs}$$

then for any t ,

$$\epsilon_{r,s}^{q,z} \epsilon_{q,z} = \epsilon_{r,s} \epsilon_{q,z}^{r,s} \quad (24)$$

From (10) and (20), the transition probabilities are given by

$$\lambda_{ij} = \frac{\sum_s \sum_x \epsilon_{i,p}^{j,x}}{\sum_s \epsilon_{i,s}(t)} \quad (25)$$

$$\lambda_{ji} = \frac{\sum_s \sum_x \epsilon_{j,p}^{i,x}}{\sum_s \epsilon_{j,s}(t)}.$$

However, the standard thermodynamical result is

$$\lambda_{ji} = \sum_r \sum_s P'_s \lambda_{ir,jr} = \sum_r \sum_s P'_s \lambda_{js,ir} \quad (26)$$

$$= \sum_r \sum_s \left(\frac{\epsilon_{js}^{ir}}{\epsilon_{js}} \right) \cdot P'_s.$$

The reservoir state is given by

$$P'_s = \left(\sum_j \epsilon_{j,s} \right) / N. \quad (27)$$

From (26) we see that

$$\lambda_{ji} = \left(\sum_q \sum_r \sum_s \left(\frac{\epsilon_{js}^{ir}}{\epsilon_{js}} \right) \epsilon_{qs} \right) / N. \quad (28)$$

We note that this is not the same as (25). Furthermore, because of the symmetry (eqn 24),

$$\lambda_{ji} = \sum_r \sum_s P'_s (\epsilon_{js}^{ir} / \epsilon_{js}) = \sum_r \sum_s P'_s \epsilon_{ir}^{js} / \epsilon_{ir} \quad (29)$$

$$= \lambda_{ij}$$

in contradiction to what was mentioned earlier [in eqs. (20) and (25)]. Thus, for modelling kinetic processes, the forms given in (25) must be used if time reversibility assumptions are not utilized since (29) would contradict the standard forms which assume symmetry (Cox 1950, p.242). Often, applications have assumed the validity of time reversed detailed balanced without further question (Ben-Shawl *et al.* 1979; Hood *et al.* 1984, Sec.V(D); Klein 1955, eqn.3; Lloyd *et al.* 1954, sec.5; Reif 1965, p.553). The description as elaborated in standard treatments is attractive because it relates the transition probabilities to the equilibrium probability density distribution, where the cardinal and oftened utilized formula (Reif 1965, eqn.5.2.10) for non-equilibrium distributions is given by

$$\frac{W_{sr}}{W_{rs}} = \frac{\exp(-\beta E_r)}{\exp(-\beta E_s)} \quad (30)$$

where the transition probabilities are no more symmetrical, and where in actuality these transitions are between a much larger thermal reservoir at a known temperature coupled to a system in equilib-

rium with it, but which is extrapolated to nonequilibrium regimes using detail balance arguments. Monte Carlo techniques have been applied with the supposition that detailed balance is a necessary condition for its algorithms, but it can be shown that this need not be the case (Jesudason 1997).

In fact, part of the above developments may be traced to the influence of the assumption that for weakly coupled systems, the probabilities of the system and thermal reservoir are independent. Such an assumption, however is not always compatible with the principle of conservation of energy and may be demonstrated as follows (Reif 1965, p.551).

Let the probability of the heat bath (which is coupled weakly to the smaller system) existing in state r' be denoted by $P_{r'}(t)$, and this probability is proportional to the factor $\exp(E_{r'}/kT)$, where $E_{r'}$ is the energy of the r' state, T the temperature and k the Boltzmann constant.

Then

$$0 \leq P_{r'}(t) \leq 1$$

and

$$\sum_{r'} P_{r'}(t) = 1 \tag{31}$$

For the system at any state i , we must have

$$\left. \begin{aligned} \sum_i P_i(t) &= 1 \\ 0 \leq P_i &\leq 1 \end{aligned} \right\} \tag{32}$$

and

$$\left[\sum_i P_i(t) \right] \left[\sum_{r'} P_{r'}(t) \right] = 1 \tag{33}$$

where the conservation of energy may be stated

$$E_{r'} + E_i = E_{total} = \text{constant} \tag{34}$$

for all states $\chi(i,r')$ of the composite system where E_{total} is the energy of the composite system. If either the system or the reservoir is observed separately, then P_i and $P_{r'}$ would represent the probabilities of the occurrence of the respective states i and r' . The terms in the expansion of the product in (33) would be of the form $P_i P_{r'}$. Since probabilities are always positive, each term in the expansion is positive.

Multiplying out (33) and supposing that $P(i,r') = P_i(t) P_{r'}(t)$ implies that a violation of the conservation of energy will ensue for state $\chi(i,r')$ when

$$E_{r'} + E_i \neq E_{total} \tag{35}$$

If we neglect those states which imply an energy violation, then summing over the probabilities of all allowed states with the assumed validity of the expression for $P(i,r')$ would lead to a total probability of occurrence less than one, which is a contradiction. To typically assume the probability of the system as a product of two independent probabilities with partial energy conservation (Hagstrum 1966, eqn.5; Hood *et al.* 1985, eqn 12; Reif 1965, eqn.15.2.4) in such systems whilst maintaining the Markovian master equation form with the added postulate of detailed balance would similarly lead to the above difficulties regarding probability of occurrence, even if the transition probabilities are symmetric with respect to permutations of the subscripted indices. It appears, therefore, that great care must be exercised in writing down kinetic equations where the probabilities are considered independent but which are nevertheless subjected to energy constraint and/or Markovian master equation forms.

In what follows, the system may be composed of weakly coupled subsystems which do not conserve total energy, *i.e.* the coupled subsystem described by the state $\chi(p,q)$ is further coupled to an energy source or sink, where all the coupled sub-systems are in the same reference state before measurements are commenced.

The theory of Markov chains (Rozanov 1977, p.84) give the master equation in standard form as

$$P_\alpha(t) = \sum_i W_{i\alpha}(t - \delta t) P_i(t - \delta t) \quad (36)$$

where i and α are general states of the system and the W 's represent the transition probabilities.

For a coupled system, the transition probabilities W^0 are given by (per unit time)

$$W^0(rr' \rightarrow ss') = \varepsilon_{r,r'}^{s,s'} / \varepsilon_{r,r'}$$

therefore

$$\begin{aligned} W^0(r \rightarrow s) &= \frac{\sum_{p'} \sum_{q'} \varepsilon_{r,p'}^{s,q'}}{\sum_{z'} \varepsilon_{r,z'}} \\ &= \frac{\varepsilon_r^s}{\sum_p \varepsilon_r^p} (\leq 1) \end{aligned} \quad (37)$$

where

$$\left. \begin{aligned} \varepsilon_{r,q'} &= \sum_p \sum_{z'} \varepsilon_{r,q'}^{p,z'} \\ \varepsilon_r^p &= \sum_{q'} \sum_{z'} \varepsilon_{r,q'}^{p,z'} \end{aligned} \right\} \quad (38)$$

From Eqns (37-38)

$$\begin{aligned} \sum_s W^0(r \rightarrow s) &= \frac{\sum_s \varepsilon_r^s}{\sum_s \varepsilon_r^p} \\ &= \sum_r^p W^0(s \rightarrow r) \\ &= 1 \end{aligned} \quad (39)$$

by permuting the super and subscripted variables.

2.3. Discussion of Various Representations

The formal definition of detailed balance is not clear, where a variety of different meanings are associated with this concept, some of which are discussed below to illustrate how contradictory statements may be avoided in deriving a form of the transition probability.

(a) On detailed balance from the master equation

Let

$$\begin{aligned} \dot{P}_n &= \sum_i [P_i W_{in} - P_n W_{ni}] \\ &= \sum_i [W_{in} (P_i - P_n)] \end{aligned} \quad (40)$$

represent a postulated master equation, where the P 's and W 's are the probabilities of state occupation and transition probabilities respectively. It is commonly believed that W_{in} equals W_{ni} because of a result in first-order time dependent perturbation theory. (Yourgrau *et al.* 1982, p.81) From (40), a steady state, such as an equilibrium state would imply that all the P 's are zero, equal or that

$$\sum_i W_{mi} P_n = \sum_i W_{in} P_i \quad (41)$$

or

$$P_n = \sum_i W_{in} P_i \quad (42)$$

since (37-38) yields

$$\sum_i W_{in} = \sum_i W_{ni} = 1$$

if

$$W_{ni} = W_{in} \quad (43)$$

where P_n is not a rate of change of a quantity; that is, there are linear dependent relations amongst the probabilities apart from the one due to normalisation.

On the other hand if detailed balance (Thomsen 1953, Section II(D)) means that for each particular state transition $i \rightarrow j$ there exists also the transition $j \rightarrow i$ such that the rates are the same at a steady state (such as thermostatic equilibrium) for each of these transitions, then for the k th state transition, the contribution to the q th state probability rate \dot{P}_q^k must vanish *i.e.*

$$\dot{P}_q^k = P_k W_{kq} - P_q W_{qk} = 0, \quad (44)$$

so that

$$P_k W_{kq} = P_q W_{qk}. \quad (45)$$

If, however, $W_{kq} = W_{qk}$ then $P_k = P_q$. Thus for such problems, the probabilities are all equal if the transition probabilities do not change. If there exists a situation in equilibrium where $P_k \neq P_q$ but where the transition probabilities are still symmetric for the equilibrium state, then a contradiction would follow, *i.e.*, detailed balance in the above sense does not hold generally. It is at this point that equations which effectively do not require symmetry of the coupling coefficients are constructed in the standard representation (Cox 1950) *i.e.* $W_{in} \neq W_{ni}$ where the energies between the states are different. Perhaps these constructs are based on the conviction that the only master equation which adequately models a system at equilibrium is represented by the Pauli type [*i.e.* eqn. (17)] and since it is known that the probabilities are not all equal at equilibrium, then the coupling coefficients cannot be symmetrical if detailed balance is demanded as a necessary condition for equilibrium. Clearly it is one thing to demand postulated conditions and another to realise that there may be other representations for equilibrium not subsumed by current hypotheses. The felt need to reconcile the symmetry of the coupling coefficients derived from traditional quantum mechanical methods (*e.g.* Fermi's Golden Rules) and the inherent non symmetry of the coupling coefficients at equilibrium (given the demand for eqn. (17) as the only form) has possibly lead to conflicting developments of detailed balance concepts, some of which are discussed below.

2.3.2 A view of events in time

Let there be a characteristic time τ to discern events *i.e.*, a situation whereby events are 'quantized' in time extension. Then there is a unit of time in which the entire class of events are contained, where the events are characterized by a particular transition $r r' \rightarrow s s'$. Let there be N different transitions. Then $I = 1$ or $\tau = 1/N$. These types of processes may be conveniently modelled after Poisson-type statistics [in any one frame of reference].

2.3.3. Elementary Quantum Mechanical Consideration

The equilibrium distribution function for a system may be derived by using the fundamental statistical postulate that the probability of any particular state is proportional to the number of states

accessible to a much larger system in thermal equilibrium with the smaller system. (Reif 1965, pp. 201-203).

However, in quantum mechanics, the probability of a system being in a state n , whose wave function is

$$\Phi(q, t) = \sum_k C_k(t) U_k(q) \exp(-2\pi i / h) E_k^0 t$$

is W_n , where

$$W_n = C_n^*(t) C_n(t) \quad (46)$$

and q and t are the system space and time co-ordinates respectively, all other notations being standard.

If the system is in state k at time $t = 0$, then the transition from state k to a group of states ν near n of density σ_n is governed to first order by the equation (Tolman 1950, pp. 400-401)

$$\dot{P}_n(t) = \frac{4\pi^2}{h} |V_{nk}|^2 \sigma_n \quad (47)$$

where V_{nk} represents the matrix element of the perturbing Hamiltonian and $\dot{P}_n(t)$ is the probability rate for the n th state.

It must be realized that the density of states is not immediately proportional to the probability of occurrence of any particular state n in a non-equilibrium situation since from (47), the probability of occurrence of the state ν is zero at time $t = 0$, in spite of its having a high density of states.

It follows that degeneracy factors are also important in constructing simple master equations for elementary kinetic processes.

Prigogine (Delgado Domingos *et al.* (eds) 1974, p. 175) has later commented [in addition to his earlier association with purely classical detail balance (Glansdorf *et al.* 1954)] that for weakly coupled systems, Onsager's proof actually reduces to Fermi's Golden Rules for transition probabilities and as such allows for more general applications. We may therefore infer that such applications will run into similar difficulties as mentioned in previous sections concerning classical considerations because it will be demonstrated that the higher order coupling coefficients in a system result from the expansion of a perfect differential by Taylor expansion, and it is difficult to establish a similar correspondence in quantum mechanical transition probabilities, although this must exist. Furthermore, in the steady state such as equilibrium, the rate of transition and probability of occupation is proportional to the degeneracy or phase space volume of the state (fundamental assumption of equilibrium statistical thermodynamics) so that in this case σ_n cannot represent a probability measure for state n (since it is empty), implying that for these processes, another type of rationalization may be required to connect quantum mechanics to non-equilibrium thermodynamics. . [If it can be established that the degeneracy or phase space volume element is always equivalent to the density σ_n then the standard expressions (such as (47)) would seem to be more firmly grounded.]

Conclusions

This part argues that the fundamental premises of time reversibility in physical theory does not directly follow from the analytical results in mechanics and statistics. There seems therefore a pressing need to found these and other physical theories on a firmer foundation than what is currently available. The sequel will attempt to suggest a few areas that may be explored. However, it is anti-

pated that such a project would require new developments in social and political relations to tap the experiences of persons in a value attributive manner (due to anamnesis of work) over a broader 'community space' of persons, if there is to be any hope of long-term coherence.

Postscript

[The sequel to this work appeared in *Apeiron* 6(3-4) : 172-185(1999) and equation (32) should have read $\alpha \cdot \delta n \cdot \delta \phi / T \geq 0$.]

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