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Focus on the Clausius Inequalities as a consequence of modeling thermodynamic systems as a series of open Carnot cycles

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ABSTRACT

Various results in thermodynamics developed recently are brought into focus by further refinement to set in less ambiguous form topics connected to irreversibility and the so called "Clausius Inequality". This singular "Clausius Inequality" for both closed and open systems was traditionally deduced from the Riemann "integration" of closed Carnot cycle loops for irreversible transitions. Evidently topological problems might be expected to arise concerning boundary conditions when "open" and "closed" systems exists simultaneously in such a scheme. It has hitherto been assumed that in this scheme, only one central Clausius Inequality can exist coupling all processes. Based on a new recent development of open system Carnot cycles, it is shown that other analogous inequalities can be derived, due to the presence of another fundamental entropy state function derived in the recent development, implying non-singularity. Their properties are such as to indicate that no new non-equilibrium entropy can arise from the inequalities as has been proposed over the decades. It is shown that a sequence of points along a non-equilibrium state space must have excess variables augmenting those for the equilibrium situation, which demonstrates that the often used Principle of Local Equilibrium (PLE) is only an approximation, implying that far-from-equilibrium theories should be developed ab initio from irreversible dynamical laws rather than from PLE. Examples presented from actual computations for both systems in equilibrium and non-equilibrium appears to support this deduction. Large scale and extensive thermodynamical theories have been created based on the assumption of a single Clausius-like inequality, such as those stemming from the very influential and extensive Truesdale school, and so such pervasive developments are also open to question.

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1. Carnot cycle analysis for open systems

Recently [1], a new development for an open system thermodynamical theory was presented, where another entropy form was shown to exist, implying that there exists at least two forms of the fundamental Clausius inequality, each form pertaining to the entropy type. Previously, from the time of the establishment of the Second Law by Clausius and others in the latter half of the nineteenth century, it was assumed that only one form existed, from which many fundamental theories were constructed that could couple all the heat and thermodynamical energy terms so that they fulfilled this inequality. That inequality also provided bounds concerning entropy production in thermodynamical systems and processes. Here, we focus and refine on the details of these inequalities which were only developed in passing previously. Clearly the current development implies a need to reassess slowly the entire structure laid in the past. Below, a resume of the new development is provided before developing the inequalities with some applications due to results from computations.

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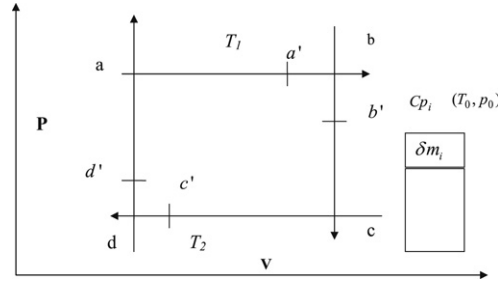
Fig. 1. A system about reversible cycle abcda.

An open Carnot system operating between two reservoirs at temperatures T_1 and T_2 are given and its properties during summation limits have been outlined [1]. A typical cycle is given in Fig. 1, where the state space $\Sigma = \{\mathbf{P}, \mathbf{V}, \mathbf{m}\}$ denote the system intensive and extensive variables and the mass amounts present, respectively; $\mathbf{m} = \{m_1, m_2 \ldots m_i \ldots m_n\}$ is the set of 'pure' substances injected into the open system; $\mathbf{m} \cup \mathbf{V}$ are the extensive quantities such that $-\mathbf{P} \cdot (\delta\mathbf{V} + \delta\mathbf{m})$ represents the work gained by the system for arbitrary displacements $(\delta\mathbf{V} + \delta\mathbf{m})$ in multidimensional space $(\mathbf{P}, \mathbf{V}, \mathbf{m})$ with mass exchange δm_i. In addition, a, b, c, d also represents the state variables Σ. The two basic cycles are C_{iso}, where mass in inserted at the isothermal segments of the Carnot cycle and C_{adia}, where they are inserted without heat exchange at the adiabatic portions. For cycles C_{iso}, $\delta Q_{a-a',sys}^{T_1}$ is the heat absorbed without mass change along $a-a'$, where masses δm_i are injected reversibly via semi-permeable membranes at constant temperature along $a'-b$ accompanied by the simultaneous exchange of heat $-\delta Q_{c-c',sys}^{T_2}$, and the heat absorbed along cc' is $-\delta Q_{cc'}^{T_2}$, and when mass is extracted at $c'd$ the heat gained by diathermal heat transfer through the boundary is $-\delta Q_{inj,i}^{T_1}$ via the system isothermal boundaries, whereas for C_{adia} cycles there is no temperature control for the system during reversible exchange of masses. The temperatures along isotherms ab and cd is T_1 and T_2, respectively; for any of these cycles, heat is exchanged with the thermal reservoirs labeled T_1 and T_2 held, respectively, at the temperatures T_1 and T_2 and there is also the work done to transport material i from the supply cell Cp_i at standard state (ss) (T_0, p_0) to the surface of the reactor cell ΔW_i^{form}, where the element δm_i is in equilibrium with the reactor cell through the semi-permeable membrane with pressure–temperature variables (p_i, T). The normal work terms in a system transition are denoted δW for transitions along state Σ when there is no mass exchange (as in a normal Carnot engine), with superscripts and subscripts indicating the transition coordinates; δW_{inj} denotes the work of injecting the specified material into the reactor cell. The total work done [1] on the environment by the system $\Delta W_{tot,iso}$ and by the heat pumps (all working cyclically) about $a \rightarrow b \rightarrow c \rightarrow d$ is

$$\Delta W_{tot,iso} = -\delta W_{aa'}^{T_1} - \delta W_{cc'}^{T_2} - \delta W_{bc} - \delta W_{da} + \delta V_{ss}^{(T_1,p_{i,b})} - \delta V_{ss}^{(T_2,p_{i,d})} + \Delta W_i^{form}(p_{i,b}, T_1) - \Delta W_i^{form}(p_{i,d}, T_2)$$

$$- \delta W_{inj}(a'b) + \delta W_{inj}(c'd). \tag{1}$$

Total heat *lost* at T_1 reservoir $\Delta Q_{1,tot,iso}$ is

$$\Delta Q_{1,tot,iso} = \delta Q_{aa',sys}^{T_1} + \delta Q_{inj,i}^{T_2} + T_1 \delta m_i \Delta \mathcal{S}_{i,ss}^{(T_1,p_i)}. \tag{2}$$

Q2 Total heat *gained* at T_2, $\Delta Q_{2,tot,iso}$ is

$$\Delta Q_{2,tot,iso} = \delta Q_{c'c,sys}^{T_2} - \delta Q_{inj,i}^{T_2} + T_2 \delta m_i \Delta \mathcal{S}_{i,ss}^{(T_2,p_{i,c'd})}$$

$$= \delta Q_{cc',sys}^{T_2} - \delta Q_{inj,i}^{T_2} + T_2 \delta m_i \Delta \mathcal{S}_{i,ss}^{(T_2,p_{i,c'd})} \tag{3}$$

where $\Delta \mathcal{S}_{i,ss}^{(T,p_i)} = \left(\int_{ss}^{(p_i,T)} \frac{dQ_i}{T} \right)$ is the convected entropy per unit mass for substance i with heat contribution deriving from the indicated reservoir. More explicitly,

$$\delta V_{ss}^{(T_1,p_1)} = \Delta V_{i,ss}^{(T,p_1)} \delta m_i = T \delta m_i \Delta V_{i,ss}^{(T,p_1)} - \Delta Q_{i,ss}^{(T,p_1)} \delta m_i$$

is the work done on the environment for the pumping mechanism of species i with mass δm_i where $\Delta Q_{i,ss} = \int_{ss}^{(p_i,T)} dQ$ and $\Delta Q_i^{(p_i,T)} = T \left(\int_{ss}^{(p_i,T)} \frac{dQ_i}{T} \right) \delta m_i = T \delta m_i \Delta \mathcal{S}_{i,ss}^{(T,p_i)}$. The corresponding results for an adiabatic C_{adia} cycle where mass is extracted or injected is (subscripted *adia.* refers to the C_{adia} cycle and similarly other subscripts refer to the path or state)

$$\Delta W_{tot,adia} = -\delta W_{ab}^T - \delta W_{cd}^{T_2} - \delta W_{b'c} - \delta W_{d'a} + \delta V_{ss}^{(T_1,p_{i,bb'})}$$

$$- \delta V_{ss}^{(T_2,p_{i,d'})} + \Delta W_i^{form}(p_{i,b}, T_1) - \Delta W_i^{form}(p_{i,d}, T_2). \tag{4}$$

$$\Delta Q_{1,tot,adia} = \delta Q_{ab,sys}^{T_1} + \delta Q_{inj,i}^{T_1} + T_1 \delta m_i \Delta \mathcal{S}_{i,ss}^{(T_1,p_i)}. \tag{5}$$

$$\Delta Q_{2,tot,adia} = \delta Q_{dc,sys}^{T_2} + \delta Q_{inj,i}^{T_2} + T_2 \delta m_i S_{i,ss}^{(T_2,p_i(c'd))}. \tag{6}$$

There is no heat absorption about an adiabatic segment. For a mixed elementary loop cycle C_{comb} where mass is injected (extracted) at an isothermal pathway e.g. *ab* and extracted (injected) at the adiabatic pathway e.g. *da*, we still derive $\Delta W_{\text{tot,comb}}$, $\Delta Q_{1,\text{tot,comb}}$ and $\Delta Q_{2,\text{tot,comb}}$, as above. For the above cycles (denoted C) operating between temperature points 1 and 2, and for general transitions the following (Theorems 1–3) have been proven [1].

Theorem 1. *Each elementary cycle C fulfills* $\frac{\Delta Q_{1,\text{tot},C}}{T_1} - \frac{\Delta Q_{2,\text{tot},C}}{T_2} = 0$ *for optimized Carnot trajectories.*

Theorem 2. *A perfect differential* $d\mathcal{S} = \frac{dQ_{\text{tot}}}{T}$ *for the state function $\mathcal{S}$ exists, given by*

$$\Delta\mathcal{S} = \frac{dQ_{\text{dia}}}{T} + \sum_{i=1}^{n} \Delta\mathcal{S}_{i,ss}^{(T_1,p_i)}\delta m_i$$

where $dQ_{\text{tot}} = dQ_{\text{dia}} + T\sum_{i=1}^{n}\Delta\mathcal{S}_{i,ss}^{(T_1,p_i)}\delta m_i$ *and* $dQ_{\text{dia}} = dQ_{\text{sys}} + \sum_{i=1}^{n} dQ_{\text{inj},i}$.
The total reversible diathermal heat transfer increment dQ_{dia} consists of dQ_{sys} which is the heat absorption by the diathermal boundary of the system when there is no mass transfer taking place and to $dQ_{\text{inj},i}$ when there is a transfer of substance i of amount δm_i.

Theorem 3. *There exists an entropic function of state $\mathcal{S}_{\text{dia}}$ with differential given by $d\mathcal{S}_{\text{dia}} = \frac{dQ_{\text{dia}}}{T}$ where Q_{dia} is a local function representing the total heat absorption of the system through a diathermal boundary as above.*

The traditional Clausius Inequality was derived using some of the following well-founded axioms.

Axiom 1. It is impossible to construct an engine working in a cycle, which will produce no other effect than the transfer of heat from a cooler body to a hotter one.

Axiom 2. The Σ variables vary continuously in the system transitions and are differentiable and in particular the **m** variables vary continuously even within a single open Carnot loop *j* which is an element in the Riemann sum, so that no finite instances of measured mass injections/extractions can occur for any *j* loop.

Axiom 3. The energy functions have perfect total derivatives i.e. they are state functions.

Axiom 4. Irreversible pathways traverse a pathway along a sequence of points exactly that of a reversible pathway where the Σ variables are concerned in an arbitrary circular, but yield different diathermal heat absorption increments for each element *j* of the Riemann summation.

As stated in the introduction, the existence of the state function $\mathcal{S}_{\text{dia}}$ implies that the form of the Clausius inequality is not obvious and must be carefully constructed based on the available facts.

Theorem 4. *The Clausius inequality corresponding to Theorem 2 for the non-local heat increment is* $\oint \frac{dQ_{\text{tot}}}{T} \leq 0$.

Proof. The optimized elementary reversible Carnot cycle yields is zero from Theorem 1 for fixed temperature of reservoirs, so that the non-optimized cycle can only be $\frac{\Delta Q_{1,\text{tot},C}}{T_1} - \frac{\Delta Q_{2,\text{tot},C}}{T_2} \leq 0$ for any elementary loop (Axiom 4). Taking N cycles ($N \to \infty$) to complete the Riemann sum for any loop yields $\lim_{N\to\infty}\sum_{j=1}^{N}\left(\frac{\Delta Q_{1,\text{tot},C,j}}{T_j} - \frac{\Delta Q_{2,\text{tot},C,j}}{T_j}\right) \leq 0 \Rightarrow \oint \frac{dQ_{\text{tot}}}{T} \leq 0$. □

The proof that follows require Axioms 1 and 2. The dQ_{tot} heat increment is a combination of local and non-local heat terms.

Theorem 5. *The Clausius Inequality corresponding to Theorem 3 is* $\oint \frac{dQ_{\text{dia}}}{T} \leq 0$.

Proof. One must consider whether optimized processes are involved or not in the partitioned local heat increment dQ_{dia} which is not similar to the non-local total heat increment dQ_{tot}, where an optimized process is involved to derive an inequality by examining the energy transfer terms with the supply cells Cp_i. Let $U_{i,um}$ be the intensive energy variable relative to the supply cell to extract unit mass of substance *i* to state Σ of the primary cell (system) at equilibrium with it through a semi-permeable membrane, so that the actual energy increment transferred to the surface prior to any work being done on it is $d\mathcal{U}_i = U_{i,um}(\Sigma)dm_i$ for substance *i*. Gibbs' integration leads to the total energy (which has a perfect differential for it is a state function) of superficial –meaning surface- transfer $\mathcal{U}$ being $\mathcal{U} = \sum_{i=1}^{m} m_i U_{i,um}(\Sigma) = \sum_{i=1}^{m} m_i\mathcal{U}_i$ where $\mathcal{U}_i = m_i U_{i,um}(\Sigma)$. Since $d\mathcal{U} = \sum_{i=1}^{m} dm_i U_{i,um}(\Sigma)$ for an *m*-substance system, another Gibbs–Duhem type equation $\sum_{i=1}^{m} m_i d(U_{i,um}(\Sigma)) = 0$ is proven to exist here. For any *j*th open Carnot engine, the energy associated with the convected mass prior to injection is written $\sum_{i=1}^{m} dm_{i,j}U_{i,um,j}(\Sigma)$ where the sign of $dm_{i,j}$ determines injection or extraction. For this cycle, the work energy to inject (extract) dm_k by the environment is $-W_{\text{inj},k,j}(\Sigma)dm_k$ and the external work done by the machine is $W_{\text{ext}}^j = \oint \mathbf{P} \cdot d\mathbf{V} + \sum_{k=1}^{m}\oint_{\partial m_k} W_{\text{inj},k,j}(\Sigma)dm_k$. In one cycle, the whole system is returned to the original state.

From Axiom 2, for the jth cycle, define $\Delta \mathcal{U}_i = \oint_m \sum_{i=1}^m dm_i U_{i,um}(\Sigma)$ where Q_1^j, Q_2^j are the total diathermal heat absorptions in this cycle at temperatures T_1, T_2, respectively. Clearly, $\Delta \mathcal{U}_i = 0$ (Axiom 3). The connection of the Q's to the diathermal entropy is $\oint d\mathcal{S} = \oint \frac{dQ_{tot}}{T} = \lim_{N \to \infty} \sum_{j=1}^N \left(\frac{Q_1^j}{T_1} - \frac{Q_2^j}{T_2} \right) = 0$. The conservation of energy for each cycle loop j (Axiom 3) is

$$\Delta \mathcal{U}_j + Q_1^j - Q_2^j - W_{ext}^j = 0. \tag{7}$$

As $j \to \infty$ to complete a loop in Σ space, $\oint d\mathcal{U}_i = \sum_{j=1}^N \Delta U_j = 0$, and so from (7)

$$\lim_{N \to \infty} \sum_{j=1}^N \Delta \mathcal{U}_j + Q_1^j - Q_2^j - W_{ext}^j = 0$$

$$\Rightarrow \oint dQ_{dia} = \oint dW_{ext} = \Delta W_{ext} \tag{8}$$

where ΔW_{ext}, the total work done by the system in any arbitrary loop in Σ space, equals the total reversible diathermal heat absorbed. The above was derived implicitly in [1] when deriving a Principle of Correlation. For each j cycle, the virtual closed Carnot engine has work done dW_{vir}^j, the maximum given by $dW_{vir}^{j,max} = Q_1^j \left(\frac{T_1^j - T_2^j}{T_1^j} \right)$ from which energy conservation gives $\frac{Q_1^j}{Q_2^j} = \frac{T_1}{T_2}$. Now, from Axiom 4, the temperatures for the virtual and real system are the same at the diathermal ends, and if Q_1^j is fixed, then so is Q_2^j. If this Q_2^j, denoted $Q_2^{j'}$ is different from the open system Q_2^j, then for this cycle running one engine against another would violate Axiom 1 for the reversible situation, hence they must be the same. Comparing with Eq. (7) yields $Q_1^j - Q_2^j = dW_{vir}^{j,max} = dW_{ext}^j - \Delta \mathcal{U}_j$, so that summing over all j loops yield for the reversible case

$$\oint dW_{vir} = \Delta W_{vir} = \oint dW_{ext} = \Delta W_{ext} \tag{9}$$

where the work done by a closed Carnot engine is precisely that of the open system; this is the Principle of Correlation developed previously [1]. If the efficiency of the irreversible engine exceeded that of the closed Carnot cycle at a particular j cycle, then as before running this system coupled to a reversible system would lead to a violation of Axiom 1. Hence if the actual work W_{ext}^j is less than the maximum reversible work for a particular j cycle $W_{ext}^{j,max}$, then $W_{ext}^j < W_{ext}^{j,max} \Rightarrow \left(\frac{Q_1^j}{T_1} - \frac{Q_2^j}{T_2} \right) < 0$ and summing this as $j \to \infty$ (as in Theorem 4) over a closed loop leads to $\oint \frac{dQ_{dia}}{T} \le 0$.   □

Two types of Clausius inequalities are derived, where the heat term in Theorem 5 is local. The above results contradicts Bhalekar's alleged proof [2a] that the inequality does not exist for open systems and also the rebuttal [2b] since no heat terms are discriminated and no proven state functions were used (only assumed), and where singular forms were assumed.

2. Theorems and applications

2.1. Non-existence of excess entropy function of state

Two types of heat increment terms are used here, both satisfying Clausius-type inequalities denoted $dQ_{[q]} : q = \{adia, tot\}$ where the *adia* subscript refers to the adiabatic heat increment, and the other to the non-local total heat increment as discussed in Theorems 4 and 5, with the associated entropy forms $d\mathcal{S}_{[q]}$ forms, respectively, where $dS_{[tot]} \equiv d\mathcal{S}$ of Theorem 2. There have been attempts by a tradition set by Eu [3a–j] and others [4a–c] over the last three decades to derive a new entropy form based on heat compensation from the Clausius inequality. Most irreversible systems are open in nature, but the theorem was derived initially using the traditional closed Clausius loop, and later with Gibbs' thermodynamical assumptions. A proof for closed systems that these new entropy forms cannot obtain was provided recently [5], and since the mathematical structure of both open and closed systems are the same as shown above, the results given in [5] may be generalized for the two q forms $q = \{adia, tot\}$ given above. For any two points $A, B \subset \Sigma$ define two pathways connecting these points in a continuous curve, P_{AB} and P'_{AB} which are along a reversible and irreversible pathway, respectively. Writing the Clausius integral as $-N_{[q]}$ and integrating between A and B for two paths P_{AB} and P'_{AB} about a closed loop yields $-N_{[q]} = \oint_{irrev} \frac{dQ_{[q]}}{T} \le 0$ or $N_{[q]} = \Delta \mathcal{S}_{[q]} - \int_{A,irr}^B \frac{dQ_{[q]}[P'_{AB}]}{T} \ge 0$ where $\Delta \mathcal{S}_{[q]} = \int_{A,rev}^B \frac{dQ_{[q]}[P_{AB}]}{T}$ is the reversible entropy change between A and B.

Lemma 1. *The variable $N_{[q]}$ must be a functional of the variable A, B and path P'_{AB}, i.e. $N_{[q]} = N_{[q]}(A, B, P'_{AB})$.*

Proof. Since $\Delta \mathcal{S}_{[q]}$ is the integral of a perfect differential, it is a function of the endpoints of the integral, and the irreversible integration along P'_{AB} is path dependent, hence the result.   □

Defining $N_{[q]} = \oint dN_{[q]}$, the above notation leads to $\oint \left(\frac{dQ_{[q]}}{T} + dN_{[q]} \right) = 0$, suggestive of a perfect differential $d\Sigma'_{[q]} = \frac{dQ_{[q]}}{T} + dN_{[q]}$. The following determines the issue.

Theorem 6. *The differential* $d\Sigma'_{[q]} = \frac{dQ_{[q]}}{T} + dN_{[q]}$ *is not exact and is non-local.*

Proof. Replacing the N, Q, S, Σ variables in Reference [5] (Sections 3(a) and 3(b)) by $N_{[q]}$, $Q_{[q]}$, $S_{[q]}$, $\Sigma'_{[q]}$ and repeating the argument for our general system here, where the algebra is isomorphous because of the proof of the Clausius inequality here for general systems, the above theorem follows since it is proven there [Eq. 13(b), 5] that $d\Sigma = \frac{dQ}{T} + dN$ in the notation of Reference [5] *is not an exact differential and furthermore is non-local.* □

Eu has offered a reconciliation in that if his entropy is viewed as coincident with the non-equilibrium entropy, then there is convergence between E.I.T. [4c, d] and his approach [p. 771; 3c].

2.2. Considerations in Principle of Local Equilibrium (PLE)

This principle [p. 23, 6a: p. 7, 6b: p. 7, 6c] states that a non-equilibrium steady state system may be locally described by variables that describe an equilibrium system, and that the heat transfer and other flux terms arise from the gradients in the equilibrium variables across the entire system. Some have suggested this principle to be very strong on the basis of a restricted simulation and other studies of particles with an interparticle potential [7a–c]. Theorem 7 shows that there are augmenting variables to irreversible systems without contradicting Axiom 4, which is used to derive the theorem. Implications are then discussed.

Theorem 7. $\exists$ *an infinite number of irreversible heat pathways* P'_{AB} *arbitrarily close to a reversible one* P_{AB} *due to augmenting variables* Δ.

Proof. Consider two diathermal pathways forming a closed loop in the sequence $A \to B \to A$ along P_{AB} and then back along the irreversible segment P'_{BA}. From Axiom 2, the loop is a Riemann sum of j open Carnot cycles, where a typical member is located about points $\{a_1, b_1, b_2, a_2\}$, where segments $(a_1, b_1) \in P_{AB}$, $(b_2, a_2) \in P'_{AB}$ and where segments $(b_1, b_2) \in b'$ and $(a_1, a_2) \in a'$ are adiabatic. Let the increment of heat absorbed along (a_1, b_1) be $Q_{1,[q]}$ at temperature T_1 and the heat absorbed (which has an implied negative sign since at this temperature T_2 the heat is ejected) about (b_2, a_2) be $Q_{2,[q]}$ for the forms $[q]$ with associated entropy $S_{[q]}$. When $q = dia$, the system refers to diathermal heat exchange about the paths P_{AB} and P'_{BA} and the work done W given below refers to the work done by the system on the environment, but when $q = tot$ a non-local form of heat transfer is implied, as with the work as given in (1)–(6). For what follows, we drop the usage of the $[q]$ subscript notation, for the analysis pertains to both. At optimal efficiency op, $Q_{1,op} + Q_{2,op} = -W_{op}$, where W_{op} is the total work done on the system about the j cycle $\{a_1, b_1, b_2, a_2\}$ and $W_{op} = Q_1(f(T_1, T_2))$. Since path (a_1, b_1) is reversible, $|Q_2(P'_{BA})|$ about (a_2, b_2) segment is $|Q_2| = Q_1 + W_{op} + \delta(a_2, b_2)$ where $\delta(a_2, b_2) > 0$ is the dissipation function about segment (a_2, b_2) and if an external field $\mathbf{F}$ is present, then $\delta(a_2, b_2, \mathbf{F}) > 0$. Excluding external forcing conditions (fields are part of the Σ coordinates), δ is not dependent on the reversible P_{AB} pathway, since $|Q_2| = Q_1(\Sigma) + W_{op}(\Sigma)$ or along the path, the differential of heat is $dQ_2 = \mathbf{H}(\Sigma) \bullet d\Sigma$ for a reversible system (e.g. for a perfect gas at an isotherm, $dQ_2 = PdV$) whereas δ is partially dependent on boundary conditions and field gradients; for if it were completely dependent on Σ only, then there would be the expression $dQ_{2,irr} = \mathbf{H}(\Sigma) \bullet d\Sigma - \delta'(\Sigma) \bullet d\Sigma = \mathbf{F}(\Sigma) \bullet d\Sigma$, implying a fixed dissipation amount with no control which would make $\mathbf{F}(\Sigma)$ indistinguishable from $\mathbf{H}(\Sigma)$ for arbitrary Σ, including when the cycle is reversible. Hence there must exist at least one control parameter λ in the dissipation function $\delta'(\Sigma, \lambda)$ and this λ becomes the extraneous variable not in Σ. On the other hand, Axiom 4 states $\exists$ a sequence of points about $(a_2, b_2) \subset P_{AB}(\Sigma_2) \subset \Sigma$ (Σ_2 represents the sequence of points for the P_{AB} path at the lower portion of the j cycle where heat Q_2 is dissipated). Thus it follows that $P'_{BA} = \{P_{BA}, \Delta\}$ where Δ are augmented variables not in Σ, so that P'_{BA} has the points in P_{BA} as a subsequence of its entire set. □ **Q3**

Corollary 1. *It is impossible for any irreversible pathway* P'_{BA} *to contain the same sequence of points as* P_{BA} *for any path* P_{BA}.

Remark 2. Theorem 7 contradicts the PLE or "local equilibrium hypothesis" as defined here since $P_{BA} \subset \Sigma$ exists for the non-equilibrium sequence, but $\exists$ also the Δ variables, where $\Delta \notin \Sigma$. Theory does not give the explicit form for Δ, but physical considerations suggests that Δ includes gradients of the Σ coordinates with respect to the space and time coordinates.

2.3. Examples from computations corroborating the above

Extensive computations have been carried out on the hysteresis dimer molecule concerning the thermodynamical distribution of variables in both the equilibrium and non-equilibrium regime [8,9] and the details of the computations may be found in these references. The system consists of 4096 atoms A that can react to form dimers A_2 according to the reaction $2A \leftrightarrow A_2$. Typically, the MD cell was divided up into 64 slabs orthogonal to the axis of the MD cell where thermostats were placed at both ends of the rectangular shaped cell to fix the temperature at those ends. In the Case 2
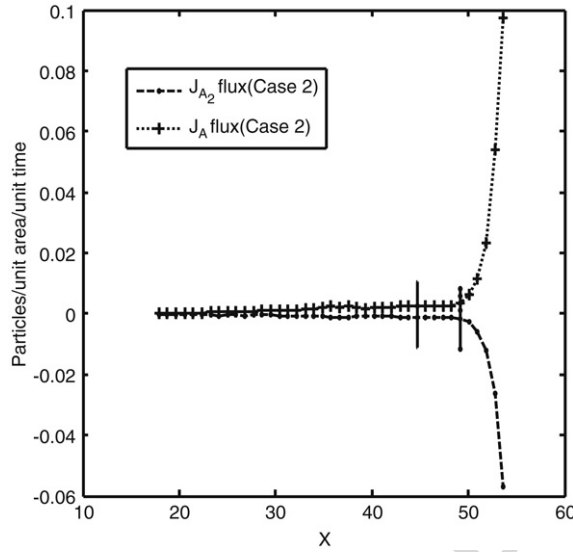
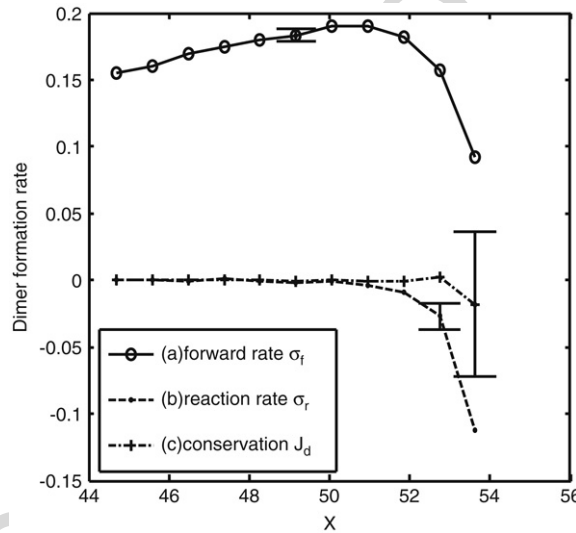**Fig. 2.** Flux currents in non-equilibrium system.

Fig. 3. Divergence of fluxes.

1   situation, the temperature is elevated at the RHS (in the vicinity of layer 64) and also all dimers were converted to atoms
2   artificially to atoms so that a steady state current flux J_A, J_{A_2} due to atoms and dimers, respectively, could be set up. As
3   pointed out in [9], the linear irreversible theory based on the principle of local equilibrium does not support the presence
4   of fluxes at the steady state. Fig. 2 shows that this theory does not obtain for large layer numbers at the RHS of the cell since
5   fluxes are clearly manifested there. To ensure that this was not an artifact, the divergence of the currents had to be worked
6   out. With stationary sources and sinks σ (σ_f and σ_b are the rate of formation and breakdown of dimer in unit time and
7   volume, respectively, throughout the cell), the conservation equations reads, respectively, $\partial c_{A_2}/\partial t = -\nabla \cdot J_{A_2} + \sigma_f - \sigma_b$ and
8   $\partial c_A/\partial t = -\nabla \cdot J_A - 2\sigma_f + 2\sigma_b$ where the c's are the concentrations. The steady state condition is $\nabla \cdot J_A = -(2\sigma_f - \sigma_b) = -2\sigma_r$
9   and $\nabla \cdot J_{A_2} = \sigma_r$ with $(\sigma_f - \sigma_b) = \sigma_r$; σ_r is a scalar flux and at thermodynamical equilibrium $\sigma_r = 0$. These equations also
10   mean $2\nabla \cdot J_{A_2} + \nabla \cdot J_A = 0$. If PLE were valid for non-equilibrium steady states, the J_A, J_{A_2} fluxes would vanish; clearly here,
11   this is not the case. To check for flux conservation, the divergence term is discretized by integration over one layer, using
12   the trapezoidal rule, where $\int_{i-1}^{i} \nabla \cdot J_{A_2} dV = \frac{(\sigma_r(i) - \sigma_r(i-1))\Delta V}{2} = J_{A_2, \text{dif}}(i) = J_{A_2}(i) - J_{A_2}(i-1)$ the layer having volume
13   ΔV. Similarly, $J_{A, \text{dif}}(i) = J_A(i) - J_A(i-1) = -(\sigma_r(i) + \sigma_r(i-1))\Delta V$; defining $J_d(i) = 2J_{A_2, \text{dif}}(i) + J_{A, \text{dif}}(i)$ leads to
14   $J_d(i) = 2J_{A_2, \text{dif}}(i) + J_{A, \text{dif}}(i) = 0$ which is a form of the divergence theorem with conservation of matter. Since the σ's are
15   all determinable, so the $J_{X, \text{dif}}$ terms can be calculated. Fig. 3 gives both the σ terms and also the $J_d(i)$ vector, which should
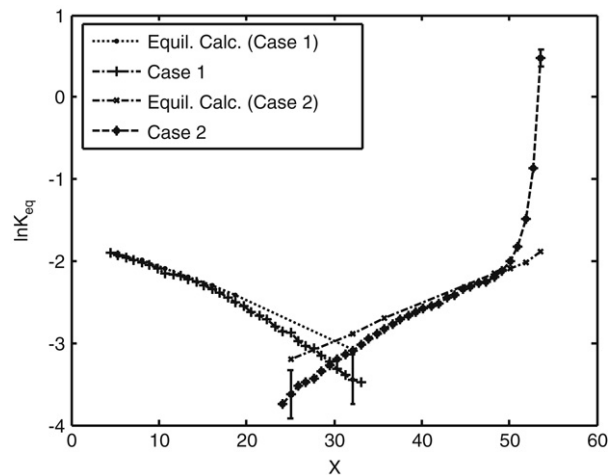16   be zero. Within experimental error, this appears to be the case.

Fig. 4. The logarithm of the equilibrium constant for equilibrium and non-equilibrium systems.

Finally, Fig. 4 is the distribution of the concentration ratio (the equilibrium constant at constant activity where $K_{eq} = \frac{[A_2]}{[A]^2}$ with two separate cases; Case 1 is where there is no breaking of bonds and where the temperature gradient is in the opposite direction to that for Case 2, where at the higher temperature reservoir (or thermostat layer) at higher layer number, an algorithm is applied that breaks bonds so as to form a current. The runs for Case 1 and 2 are separate, but plotted on the same graph for economy, they do not have the same temperature gradient distribution and hence there is an intersection in the middle portion of the graph due to this fact. In Fig. 4, the actual K_{eq} for the non-equilibrium run is plotted with the values derived from a strictly equilibrium run. Within experimental error, we observe that there is reasonable coincidence of the equilibrium and non-equilibrium runs except for Case 2 at high temperature (corresponding to higher layer value as well in this case). At low temperatures, K_{eq} is very low and therefore highly inaccurate with a large fluctuation in value. If the principle of local equilibrium is always true, then there would be coincidence even at this regime, which is clearly not the case. We hold that these results are consistent with the theory that we have developed here.

In a recent mesoscopic rendering [7b], the ambiguous Gibbsian equations [1] presuming the validity of PLE was utilized to model "far from equilibrium" situations, in contrast to Theorem 7 and a related work also presumes this by the remark: "The surprising finding is that we shall need the assumption of local electrochemical equilibrium in the reaction coordinate space" [p. 13471; 10a]. Indeed, the application is "set up by non-equilibrium thermodynamics" [p. 9170; 10b] where "non-equilibrium thermodynamics" specifically refers there to the PLE adhering, linear theory described in [6a].

3. Concluding remarks

The above results were derived by first developing the Clausius Inequalities for a multicomponent thermodynamical theory. The results were then used demonstrate that (i) that the PLE is not fundamental and (ii) that the large scale development and publication of supposedly new non-equilibrium entropies and state functions thought to arise from the Clausius inequality through a compensated heat term is largely incorrect. An allied concept is that introduced by Truesdale [11] termed the "Clausius-Duhem" inequality which forms the basis of his very influential "rational thermodynamics" which is expressed in the form

$$\frac{d}{dt}H \geq -\int_{\partial P} \frac{\mathbf{q.n}}{\theta} da + \int_P \frac{r}{\theta} dm,$$

with $H = \int_P \eta dm$ being the total entropy of part P, θ the thermodynamical temperature, $\mathbf{q}$ the heat flux to the surface ∂P with unit normal $\mathbf{n}$ and r the "external" heat supply. Benofy and Quay have criticized this form as contradictory to the Fourier inequality [12] and Second Law statements; of interest here is that a singular "total entropy" is postulated without proof by Truesdale and all other specialists, and which is not in accord with the current development. The other feature is the manner in which heat is introduced into the system by "puncturing" the surface, so that a well-defined boundary does not exist between system and environment at all times. Most of the world's literature on thermodyamics by specialists are based on *ad hoc* postulates backed by complex algebra and differential equations without being rooted in fundamental and obvious observations, such as to be found in the original statements of Planck, Clausius and Kelvin. Here the Inequalities are precisely stated and provides a basis for a much needed elaboration that this current rudimentary development lacks.

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