

“Reversibility” and Entropy History Independence

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Abstract

According to the explicit propositions by Clausius, in the original publications in the 1850's, the temperatures of the “reservoirs” are irrelevant for the “second fundamental equation” of the “mechanical theory of heat” to hold true.

It is shown that entropy being history independent, i.e., “path independent”, “state function”, is contradictory to “reversibility”, i.e., contradictory to the “second fundamental equation” of the “mechanical theory of heat” holding true for “reversible” phenomena, only.

This result is corroborated by experimental evidence.

This result only removes the unnecessary restriction posed by “reversibility”, causes no adverse practical consequences, and offers the possibility to unify and simplify continuum entropy modeling.

For example, the result removes the dilemma due to “reversibility” from engineering calculations for real physical phenomena, none of which are “reversible”.

Topical Heading and Key Words.

Thermodynamics and Molecular-Scale Phenomena

reversibility, irreversibility, entropy history independence, second fundamental equation, contradiction

1 BACKGROUND

According to Clausius¹⁻⁵, the “second fundamental equation” of the “mechanical theory of heat”

$$dS = \frac{dQ}{T}, \quad (\text{II})$$

has the *domain* restricted to “reversible” phenomena and phenomena with *non-zero temperature difference* or *heat generation* are not “reversible”. Clausius¹⁻⁵ does not explicate any justification for these restrictions.

The restriction to zero temperature difference may be based on Clausius¹⁻⁵, analogously to Carnot⁶, considering (working fluid) heat engines with the assumption of “reservoirs” with temperatures equal to the temperatures of the working fluid during the isothermal steps. The assumption is used, perhaps, to make the isothermal steps plausible – given the level of technology and engineering at the time of writing.

However, the temperatures of the “reservoirs” are *irrelevant* for the validity of equation (II), Clausius¹, p. 501, (underlines added):

“In diesem Falle ist es natürlich einerlei, ob die in der Gleichung (II) vorkommende Gröfse die Temperatur des eben benutzten Wärmereservoirs oder die augenblickliche Temperatur des veränderlichen Körpers darstellt, da beide gleich sind. Hat man aber einmal für t die letztere Bedeutung eingeführt, so ist leicht zu sehen, dafs man nun den Wärmereservoiren beliebige andere Temperaturen beilegen kann, ohne dafs dadurch der Ausdruck $\int dQ/T$ irgend eine Aenderung erleidet, welche die Gültigkeit der vorigen Gleichung beeinträchtigen könnte. Da bei dieser Bedeutung von t die einzelnen Wärmereservoirs nicht mehr besonders berücksichtigt zu werden brauchen, so pflegt man auch die Wärmemengen nicht auf sie, sondern auf den veränderlichen Körper zu beziehen, indem man angiebt, welche Wärmemengen der Körper während seiner Veränderungen nach einander aufnimmt oder abgiebt. [...]. Es ergibt sich also aus dieser Betrachtung, dafs, wenn man für jede Wärmemenge dQ , welche der Körper während seiner Veränderungen aufnimmt, oder wenn sie negativ ist abgiebt, die Temperatur in Rechnung bringt, welche er selbst im Momente der Aufnahme oder Abgabe hat, man die Gleichung (II) anwenden kann, ohne sich darum zu bekümmern, wo die Wärme herkommt oder hingeht, [...]”

Clausius³, p. 130, (underlines added):

“In this case it is of course of no importance whether t , in the equation (II), represents the temperature of the reservoir of heat just employed, or the momentary temperature of the changing body, inasmuch as both are equal. The latter signification being once adopted, however, it is easy to see that any other temperatures may be attributed to the reservoirs of heat without producing thereby any change in the expression $\int dQ/T$ which shall be prejudicial to the validity of the foregoing equation. As with this signification of t the several reservoirs of heat need no longer enter into consideration, it is customary to refer the quantities of heat, not to them, but to the changing body itself, by stating what quantities of heat this body successively receives or imparts during its modifications. [...] From what has just been said, it follows, therefore, that when for every quantity of heat dQ , which the body receives or, if negative, imparts during its changes, the temperature of the body at the moment be taken into calculation, the equation (II) may be applied without further considering whence the heat comes or whither it goes, [...]”

Clausius⁴, p. 110-111, (underlines added):

In diesem Falle ist es natürlich einerlei, ob man die Temperatur einer übergehenden Wärmemenge der Temperatur des Wärmereservoirs oder der augenblicklichen Temperatur des veränderlichen Körpers gleichsetzen will, da beide unter einander übereinstimmen. Hat man aber einmal die letztere Wahl getroffen, und festgesetzt, dass bei der Bildung der Gleichung(VII.) für jedes Wärmeelement dQ diejenige Temperatur in Rechnung gebracht werden soll, welche der veränderliche Körper bei seiner Aufnahme gerade hat, so kann man nun den Wärmereservoirs auch beliebige andere Temperaturen zuschreiben, ohne dass dadurch der Ausdruck $\int dQ/\tau$ eine Aenderung erleidet. Bei dieser Bedeutung der vorkommenden Temperaturen kann man also die Gleichung (VII.) als gültig betrachten, ohne sich darum zu bekümmern, wo die von dem veränderlichen Körper aufgenommene Wärme herkommt oder die von ihm abgegebene Wärme hingehet, [...].”

Clausius⁵, p. 106, (underlines added):

“In this case it is obviously the same thing whether we consider the temperature of a quantity of heat which is being transferred as being equal to that of the reservoir or of the variable body, since these are practically the same. If however we choose the latter and suppose that in forming Equation VII. every element of heat dQ is taken of that temperature which the variable body possesses at the moment it is taken in, then we can now ascribe to the heat reservoirs any other temperatures we please, without thereby making any alteration in the expression $\int dQ/\tau$. With this assumption as to the temperatures we may consider Equation VII as holding, without troubling ourselves as to whence the heat comes which the variable body takes in, or where that goes which it gives off, [...].”

These quotations indicate a contradiction with phenomena with *non-zero temperature difference* being excluded from the *domain* of the “second fundamental equation” of the “mechanical theory of heat”.

2 INTRODUCTION

According to Clausius¹⁻⁵, the “second fundamental equation” of the “mechanical theory of heat”

$$dS = \frac{dQ}{T}, \quad (\text{II})$$

has the *domain* restricted to “reversible” phenomena and phenomena with *non-zero temperature difference* or *heat generation* are not “reversible”.

According to Clausius¹⁻⁵, entropy is “a magnitude which depends only on the present existing condition of the body, and not upon the way by which it reached the latter”, i.e., *entropy is history independent* (“path independent”, “state function”).

Now, these may be taken to lead to dilemmas – for both students and engineers.

2.1 Student’s Dilemma – Conceptual Contradiction

Textbooks routinely consider entropy history independence in the context of equation (II).

Consider the expression:

The integral of dQ/T has the same value for *any process* between two states. In other words, the value of the integral depends on the two states, *only*.

This seems logically valid: If the integral has the same value for *any process* between the two states, then the integral *does depend* on the two states, *only* – and *does not depend* on the attributes of the process.

However, Moran et al.⁷, p. 174, (underline added):

[...] the integral of $\delta Q/T$ has the same value for *any internally reversible* process between the two states. In other words, the value of the integral depends on the end states *only*.”

This seems contradictory: If the integral “has the same value for *any internally reversible* process between the two states”, then the integral *does not depend* “on the end states only” – but *depends on* whether the process is “internally reversible” or not (because the quotation implies that for not “internally reversible” processes, the integral has not “the same value”ⁱ).

That the words “internally reversible” are deliberate and not redundant, is implied in Moran et al.⁷, p. 174, (underline added):

“Selecting the symbol S to denote this property, which is called *entropy*, the **change in entropy** is given by

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T} \right)_{\text{int rev}} \quad (6.2a)$$

where the subscript “int rev” is added as a reminder that the integration is carried out for any internally reversible process linking the two states.”

The same conceptual contradiction – or use of redundant words – is ubiquitously seen in textbooks.

This is the student’s dilemma.

2.2 Engineer’s Dilemma – Practical Contradiction

Engineering calculations routinely consider phenomena with *non-zero temperature difference* or *heat generation* in the physical reality – none of which are “reversible”.

First, consider isobaric, lossless heating of pure nitrogen from $p_1 = 1.0$ bar, $T_1 = 0.0$ C to $T_2 = 100$ C with 3 bar saturated steam ($T = 134$ C).

The first case calculated using Aspen Plus[®], of Aspen Technology, Inc., is presented in figure 1.

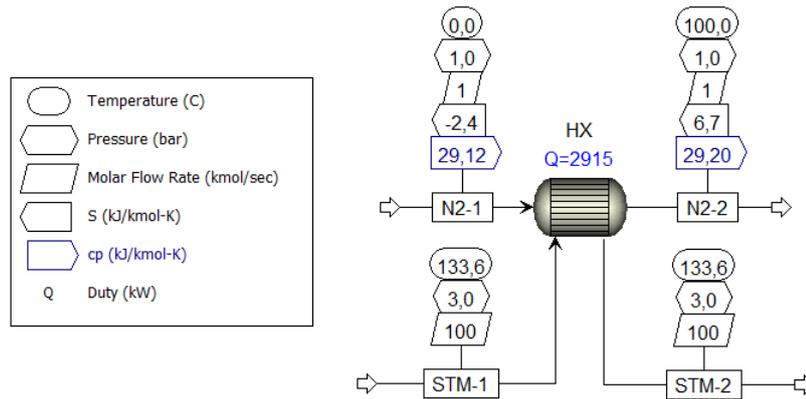


Figure 1 Non-zero temperature difference

Second, consider adiabatic, lossless compression of pure nitrogen from $p_1 = 1.0$ bar, $T_1 = 0.0$ C to $p_2 = 3.0$ bar and the same with losses with efficiency of 0.5.

The second case calculated using Aspen Plus[®], of Aspen Technology, Inc., is presented in figure 2.

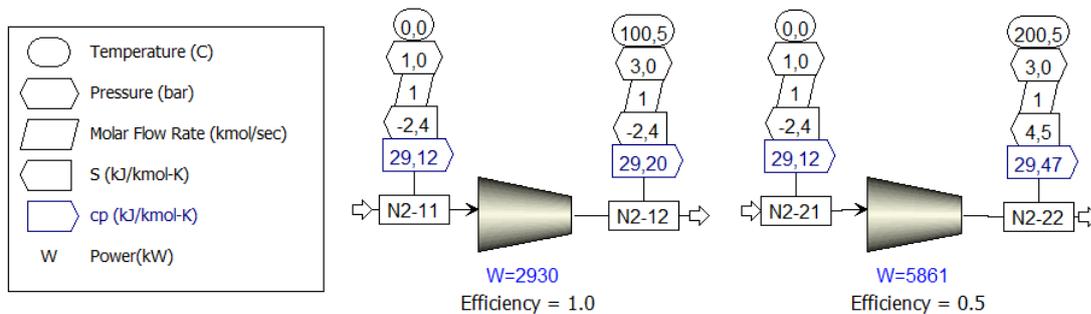


Figure 2 Heat generation

The first case calculated using the “reversible” entropy model, i.e. equation (II) – independently of the temperature of the heat source – gives

$$\Delta S = \int_0^Q \frac{dQ}{T} = \int_0^Q \frac{dQ_{ABS}}{T} = \int_0^Q \frac{dQ_{IN}}{T} = \int_{T_1}^{T_2} \frac{C_p dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right) = 9,1 \text{ J/K/mol} \quad (1)$$

It is seen that the result for ΔS is the same as calculated by Aspen Plus[®], in figure 1.

The second case – with losses, i.e., with heat generation – calculated using the “reversible” entropy model, i.e. equation (II), gives

$$\Delta S = \int_0^Q \frac{dQ}{T} = \int_0^Q \frac{dQ_{ABS}}{T} = \int_0^Q \frac{dQ_{GEN}}{T} = \int_{T_{2,lossless}}^{T_2} \frac{C_p dT}{T} = C_p \ln\left(\frac{T_2}{T_{2,lossless}}\right) = 6,9 \text{ J/K/mol} \quad (2)$$

It is seen that the result for ΔS is the same as calculated by Aspen Plus[®], in figure 2.

Thus, the numerical results obtained by the “reversible” entropy model, i.e. equation (II), conform with the results of entropy modeling in engineering practice for *non-zero temperature difference* and *heat generation* – explicitly excluded from the domain of the “reversible” entropy model, i.e. equation (II), Clausius¹⁻⁵.

This is the engineer’s dilemma.

3 “REVERSIBILITY” AND ENTROPY HISTORY INDEPENDENCE

3.1 Entropy History Independence

According to Clausius^{2,3,4,5}, p. 387, p. 355, p. 111, p. 90, entropy is “a magnitude which depends only on the present existing condition of the body, and not upon the way by which it reached the latter”, i.e., *entropy is history independent* (“path independent”, “state function”).

3.2 The Domain of the “Second Fundamental Equation”

According to Clausius^{2,3,4,5}, p. 387, p. 355, p. 114, p. 110, the “second fundamental equation” of the “mechanical theory of heat”

$$dS = \frac{dQ}{T}, \quad (\text{II})$$

has the domain of “reversible” phenomena, which may be expressed as

$$dS_{\text{"rev"}} = \frac{dQ_{\text{"rev"}}}{T}. \quad (3)$$

This entails that the domain of equation (II) excludes not “reversible” phenomena, which may be expressed as

$$dS_{\text{not "rev"}} \neq \frac{dQ_{\text{not "rev"}}}{T}. \quad (4)$$

3.3 Contradiction

For two systems with the same initial, uniform temperature T experiencing the same amount of heat associated with different phenomena, “reversible” and not “reversible”, respectively,

$$dQ_{\text{"rev"}} = dQ_{\text{not "rev"}}, \quad (5)$$

equations (3) and (4) entail that

$$dS_{\text{"rev"}} \neq dS_{\text{not "rev"}}, \quad (6)$$

which contradicts entropy history independence.ⁱⁱ

The result is *independent* of the definition of “reversibility”.ⁱⁱⁱ

3.4 Axiom

The analysis shows that the restriction of the “second fundamental equation” of the “mechanical theory of heat”, equation (II), to “reversible” phenomena contradicts entropy history independence.

Abandoning entropy history independence – abandoning that the value of entropy depends on the “state” (on the values of the “state variables” sufficient to specify the “state” uniquely), only – seems not possible.

Accordingly, entropy history independence is taken as an *axiom*.

3.5 “Reversibility”

According to the *axiom of entropy history independence*, the *domain* of the “second fundamental equation” of the “mechanical theory of heat”, equation (II), is not restricted to “reversible” phenomena.

This entails a mistake about the *domain* of equation (II) – but not about equation (II), which is the single most important equation in entropy modeling, *as such* – in Clausius¹⁻⁵ and, thus, that “reversibility”, as an restriction of the domain of equation (II), is false.

Accordingly the domain of equation (II) is the whole *scope* of the “mechanical theory of heat”, i.e., *all heat and work phenomena of closed systems*.^{iv}

3.6 Corroboration

The result is corroborated by conceptual experiments, which may be approached arbitrarily close in the physical reality, and by the equivalence of the equations of the “reversible” and “irreversible” entropy model.

In addition, the result is corroborated – implicitly, but strongly – by the *non-existence* of experimental/observational evidence for equation (II) holding true for “reversible” phenomena, *only*, i.e., by the *non-existence* of experimental/observational evidence for equation (II) *not holding true for not “reversible” phenomena*.

3.7 Practical Consequences

The falsity of “reversibility”, i.e. the elimination of the restriction of the domain of equation (II), has no adverse practical consequences, because the entropy values remain unchanged.

4 EXPERIMENTAL CORROBORATION

According to the axiom of entropy history independence, the *domain* of the “second fundamental equation” of the “mechanical theory of heat”, equation (II),

$$dS = \frac{dQ}{T}, \quad (\text{II})$$

is not restricted to “reversible” phenomena, but is rather the whole *scope* of the “mechanical theory of heat”, i.e., all heat and work phenomena of closed systems.

It is shown, next, that conceptual experiments – which may be approached arbitrarily close in the physical reality – corroborate this result.

4.1 Temperature Difference

Consider two processes to heat a solid cube from initial, spatially uniform, temporally constant temperature T_1 to final, spatially uniform, temporally constant temperature T_2 , as in figure 3.

In case a) by increasing, with *zero time-rate*, the temperature of one side of the body from T_1 to T_2 .

In case b) by fixing one side of the body to constant temperature T_2 .

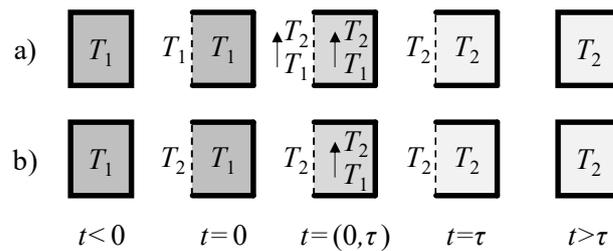


Figure 3 Heating of a Body

Because in case a) the heat transfer is with *zero temperature difference*, case a) is not excluded from the domain of equation (II) – according to Clausius¹⁻⁵.

Because in case b) the heat transfer is with *non-zero temperature difference*, case b) is excluded from the domain of equation (II) – according to Clausius¹⁻⁵.

According to the specification, the only relevant “state variable” temperature has the spatially uniform, temporally constant initial and final values of T_1 and T_2 in both cases a) and b).

Thus, according to the axiom of entropy is history independence, the final, spatially uniform, temporally constant specific entropy of the body is the same in both cases and the entropy change – and the final entropy – of the body is the same in both cases and equation (II) must hold true for both cases as

$$\Delta S = \int_0^Q \frac{dQ}{T} = \int_0^Q \frac{dQ_{ABS}}{T} = \int_{T_1}^{T_2} \frac{mc_p dT}{T} = mc_p \ln \frac{T_2}{T_1}. \quad (7)$$

This entails that the domain of equation (II) does not exclude phenomena with non-zero temperature difference.

4.2 Heat Generation

Consider the isothermal expansion of an ideal gas within a closed system from an initial, spatially uniform, temporally constant state (p_1, V_1, T_1) to a final, spatially uniform, temporally constant state (p_2, V_2, T_1) , as in the cases in figure 4.

In case a) with heat transfer with *zero temperature difference*, in case b) with heat generation due to work transfer turning a mixer with *zero time-rate*, in case c) with heat transfer with *non-zero temperature difference*, and in case d) with heat generation due to work transfer turning a mixer with *non-zero time-rate*.

For isothermal expansion of an ideal gas between the initial and final, spatially uniform, temporally constant states, $i = (a, b, c, d)$,

$$W_{OUT,i} = Q_{ABS,i} = Q_{IN,a} = Q_{IN,c} = W_{IN,b} = W_{IN,d} = Q_{GEN,b} = Q_{GEN,d} \cdot \quad (8)$$

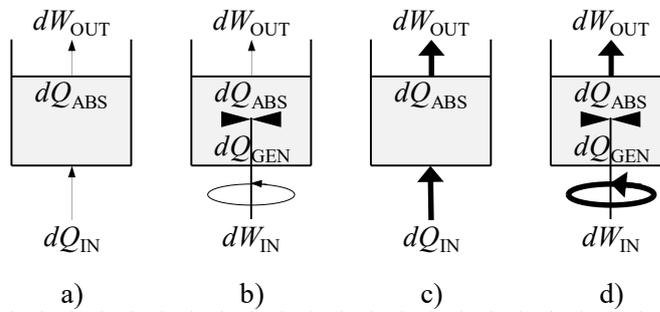


Figure 4 Isothermal Expansion

Because in case a) the heat transfer is with zero temperature difference, case a) is not excluded from the domain of equation (II) – according to Clausius¹⁻⁵.

Because in cases b) and d) the heat absorbed is *heat generated* and in case c) the heat transfer is with *non-zero temperature difference*, cases b), d), and c) are excluded from the domain of equation (II) – according to Clausius¹⁻⁵.

According to the specification, the relevant “state variables” have the spatially uniform, temporally constant initial and final values of (p_1, V_1, T_1) and (p_2, V_2, T_1) in all four cases a), b), c), and d).

Thus, according to the axiom of entropy is history independence, the final, spatially uniform, temporally constant specific entropy of the body is the same in all four cases and the entropy change – and the final entropy – of the body is the same in all four cases and equation (II) must hold true in all four cases as

$$\Delta S_a = \int_0^Q \frac{dQ_{ABS,a}}{T_1} = \int_0^Q \frac{dQ_{IN,a}}{T_1} = \frac{Q_{IN,a}}{T_1}, \quad (9)$$

$$\Delta S_b = \int_0^Q \frac{dQ_{ABS,b}}{T_1} = \int_0^Q \frac{dQ_{GEN,b}}{T_1} = \frac{Q_{GEN,b}}{T_1} = \frac{W_{IN,b}}{T_1}, \quad (10)$$

$$\Delta S_c = \int_0^Q \frac{dQ_{ABS,c}}{T_1} = \int_0^Q \frac{dQ_{IN,c}}{T_1} = \frac{Q_{IN,c}}{T_1}, \quad (11)$$

$$\Delta S_d = \int_0^Q \frac{dQ_{ABS,d}}{T_1} = \int_0^Q \frac{dQ_{GEN,d}}{T_1} = \frac{Q_{GEN,d}}{T_1} = \frac{W_{IN,d}}{T_1}, \quad (12)$$

which, with equation (8) lead to

$$\Delta S_a = \Delta S_b = \Delta S_c = \Delta S_d. \quad (13)$$

This entails that the domain of equation (II) does not exclude phenomena with heat generation or non-zero temperature difference.

5 EQUIVALENCE

5.1 Equivalence

There are currently two – main – continuum models of entropy: a “reversible” entropy model of Clausius¹⁻⁵ and an “irreversible” entropy model of Onsager⁸, Prigogine⁹, and others.

In the “irreversible” entropy model, the entropy balance for the *scope* of the Clausius’s “mechanical theory of heat”, i.e., for *heat and work phenomena of closed systems*, is, de Groot and Mazur¹⁰, p. 24,

$$\frac{\partial(\rho s)}{\partial t} = -\nabla \cdot \left(\frac{\tilde{\mathbf{Q}}''}{T} \right) - \frac{1}{T^2} \tilde{\mathbf{Q}}'' \cdot \nabla T + \frac{\tilde{Q}_{GEN}'''}{T}, \quad (14)$$

in which ρ is mass per volume, s is entropy per mass, t is time, $\tilde{\mathbf{Q}}''$ is time-rate of heat transfer per area, T is temperature, and $\tilde{Q}_{GEN}''' = -(\boldsymbol{\tau} : \nabla \tilde{\mathbf{v}})$ is time-rate of heat generation per volume due to “dissipation” of mechanical energy, Bird et al.¹¹, pp. 81-82, 213-216 – and in which a tilde is used to denote a time-rate of a quantity and primes are used to signify a quantity per area or volume.

Because heat Q , *as such*, does not exist (has no value, has zero value), *by definition*, e.g. Blundell and Blundell¹², p. 13, the three heat quantities of heat absorption Q_{ABS} , heat transfer \mathbf{Q} , and heat generation Q_{GEN} must obey,

$$\tilde{Q}_{ABS}''' = -\nabla \cdot \tilde{\mathbf{Q}}'' + \tilde{Q}_{GEN}''' . \quad (15)$$

The manipulation of equation (14) and the insertion of equation (15) gives

$$\frac{\partial(\rho s)}{\partial t} = \frac{\tilde{Q}_{ABS}'''}{T} . \quad (16)$$

Equation (16) may be expressed, for an integral system, as

$$\frac{dS}{dt} = \frac{\tilde{Q}_{ABS}'''}{T}, \quad (17)$$

and, time implicitly, as

$$dS = \frac{dQ_{ABS}}{T}, \quad (18)$$

and, finally, as

$$dS = \frac{dQ}{T}. \quad (II)$$

This demonstrates that equations (14) and (II) are equivalent, given equation (15).

Equations (14) and (II) predict the same change of entropy – and, thus, the same value of entropy.

5.2 “Local Equilibrium”

Equation (14) is taken to be not restricted to “reversible” phenomena and adequate for continuum phenomena outside equilibrium assuming “local equilibrium”, e.g., de Groot and Mazur¹⁰, p. 23:

“It will now be assumed that, although the total system is not in equilibrium, there exists within small mass elements a state of ‘local’ equilibrium, for which the local entropy s is the same function [...] of u , v and c_k as in real equilibrium.”

“This hypothesis of ‘local’ equilibrium can, from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it.”

The adequacy of the assumption of “local equilibrium” in the modeling of *any given phenomena* depends on the physical reality and not on the conceptual modeling context, whether “irreversible” or “reversible”.

Now, consider field equations of temperature and specific entropy, for a case with no heat generation and constant physical properties, of

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot \tilde{\mathbf{Q}}", \quad (19)$$

$$\rho \frac{\partial s}{\partial t} = \frac{-\nabla \cdot \tilde{\mathbf{Q}}"}{T}. \quad (20)$$

The concept of “local equilibrium” is used to justify field equations of specific entropy, as in equation (20).

In addition, field equations of specific entropy, as in equation (20), may be justified by the ubiquitous use of field equations of temperature, as in equation (19), and the analogous statistical nature of entropy and temperature, Landau and Lifshitz¹³, p. 35.

Further, field equations for “[m]otion, stress, energy, entropy, and electromagnetism” are justified as “phenomenological”, by Truesdell and Toupin¹⁴, pp. 226-233.

Accordingly, because of the equivalence, if equation (14) is not restricted to “reversible” phenomena and adequate for continuum phenomena outside equilibrium, then equation (II) is not restricted to “reversible” phenomena and adequate for continuum phenomena outside equilibrium.

6 SUMMARY

It is shown that the restriction of the domain of the “second fundamental equation” of the “mechanical theory of heat” of Clausius¹⁻⁵, equation (II),

$$dS = \frac{dQ}{T}, \quad (\text{II})$$

to “reversible” phenomena contradicts entropy is history independence.

The *axiom of entropy history independence* entails that the *domain* of equation (II) is the whole *scope* of the “mechanical theory of heat”, i.e., all heat and work phenomena of closed systems, including phenomena with *non-zero temperature difference* or *heat generation*.

The result is implied by explicit propositions by Clausius¹⁻⁵, in the original publications in the 1850’s.

The result is implied by conceptual contradictions in textbooks.

The result is corroborated by experimental evidence of engineering calculations, consistently found to conform to the physical reality.

The result is corroborated by conceptual experiments, which may be approached arbitrarily close in the physical reality.

The result is corroborated by the equivalence of the equations of the “reversible” and “irreversible” entropy model with respect to entropy accumulation and, thus, with respect to entropy values.

The result is corroborated by the *non-existence* of experimental/observational evidence for equation (II) *not holding true for not “reversible” phenomena*.

The falsity of “reversibility”, i.e. the elimination of the restriction of the domain of equation (II), has no adverse practical consequences, because the entropy values remain unchanged – but leads to theoretical and practical simplification of continuum entropy modeling.

For example, the result removes the dilemma due to “reversibility” from engineering calculations for real physical phenomena, none of which are “reversible”.

Plain Language Summary

To be delivered, if needed (for marketing purposes).

Graphical Abstract

To be delivered, if needed (for journal’s table of abstract).

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- ⁱ If the integral has “the same value” for not “internally reversible” processes, also, the words “internally reversible” are redundant and thus misleading – while not outright erroneous.
 - ⁱⁱ In the ubiquitously presented equivalent of equation (3), the subscript is expressed in the RHS, only. Following this convention in equation (4) gives equation (6) as $dS \neq dS$, which entails the same conclusion.
 - ⁱⁱⁱ As a specific example, however, one may take that $dQ_{\text{rev}} = dQ_{\Delta T=0}$ and $dQ_{\text{not rev}} = dQ_{\Delta T \neq 0}$, based on Clausius¹⁻⁵.
 - ^{iv} Equation (II) does not hold true for other than heat and work phenomena (e.g., reactions, mixing, ...) or for open systems – not because of “reversibility” but because of the *scope* of the “mechanical theory of heat” of Clausius¹⁻⁵. Equation (II) may be extended to other than heat and work phenomena and open systems.