Review of: "Classical Thermodynamics: Primacy of Dissymmetry Over Free Energy"

Truls Gundersen[1]

1 Norwegian University of Science and Technology

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Lin-Shu Wang

“Classical Thermodynamics: Primacy of Dissymmetry over Free Energy”

General Comments

Before giving comments to this paper, I need to explain my own background. Although having a PhD in Chemical Engineering with some (but not deep) exposure to Chemical Engineering Thermodynamics, my main expertise is in Mechanical Engineering Thermodynamics. I assume this is what the author refers to as "Engineering Thermodynamics". On this background, I have to admit that I struggled to fully understand the "message" of the paper.

The most important reasons for my "struggle" are related to the presenting nature:

• The language is of a poor quality with incomplete sentences.

• The terms/words used are rarely used in scientific writing (see thee Detailed Comments

section), and some of them are not even available in my dictionary.

• The paper is poorly structured and provides little guidance to the reader.

• There are many repetitions in the paper that could have been avoided or at least reduced

with a better overall structure of the paper.

There are also issues of a thermodynamic nature that I would like to discuss with the author:

• The concept of Exergy is important in Engineering Thermodynamics (in particular for

Mechanical Engineering Thermodynamics). This term is found for the first time on page 30

of the 34 pages paper. Instead, the term "Available Energy" is used. The author also in line 1

of the Abstract indicates that "Free Energy" is the same as "Available Energy".

• In Mechanical Engineering Thermodynamics, we use two terms/concepts that are closely

linked to the 2nd Law of Thermodynamics; Entropy and Exergy. Irreversibilities in a

process results in entropy production and exergy losses, and these are mathematically linked through the simple relation Exergy Destruction = T0 multiplied by Entropy Generation,

where T0 is the ambient temperature. I am curious whether the notion "dissymmetry" in the

paper is related to this "opposite" behavior of entropy and exergy?

• The most important (and surprising) error the author is making is related to the discussion in Section 2 about reversibility, internal reversibility and "quasi-staticity". I assume the last

term is equivalent to "quasi-equilibrium" that is used in several textbooks on Engineering

Thermodynamics. In particular, Equation (8) is said to "hold under the condition of quasi-staticity".

This is not correct. As explained in the Detailed Comments section, this equation

is always correct whether the process is reversible or irreversible. In Engineering

Thermodynamics, this equation is referred to as the fundamental property relation.

• In Engineering Thermodynamics, open/flowing systems are more common (and of a

considerably larger industrial interest) than closed systems. The paper uses the terms

enthalpy and internal energy side by side without mentioning the type of system assumed.

On Page 3, line 10, the text should be expanded to "Let us start with the first law for closed

systems".

• This reviewer feels there is considerable scope for improvements in the discussion about

fundamental relations, equations of state, canonical sets and potentials, and how these

preserves (or not) the "complete knowledge". It is well known that there are a number of

energy functions in Thermodynamics, such as U(S,V,N), H(S,-p,N), A(T,V,N) and G(T,-p,N).

These four are equal as far as information content is concerned. They can all be derived

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from one selected "potential", such as U(S,V,N) or S(U,V,N). These functions do not have

freely chosen sets of variables; they are equipped with unique canonic sets of variables. This is the result of Legendre transformations.

• On Page 27, line 34, the expression (HR0 - HP0) - T0 (SR0 - SP0) is the change in thermomechanical exergy (in this manuscript referred to as available energy). I must admit that I have never seen the second term interpreted as unavailable energy.

Other comments of a general type are listed below:

• There is a lot of historic references in the paper that I would assume is valuable for readers (including myself to some extent) with a keen interest in the basis for developments in Thermodynamics. As in many sciences, there are different schools of thought.

• The name/scientist Caratheodory is barely used in Classical Thermodynamics. Despite this fact, the author suggests naming important equations in Thermodynamics after this historic person. While this is refreshing, I do not think this is a good idea.

• Figures 4 and 5 and the corresponding text are hard to understand. I notice that the strangely shaped body to the right of the figures has changed position from Figure 4 to Figure 5. Also, I do not know what a "weight-cam" is. I also notice that the two systems (1) and (2) have the same number of moles N.

• With reference to Page 18, line 16, I would personally hesitate to make reference to

Wikipedia in scientific writing.

• I understand that this publication is different from regular journals, however, I still find it

strange to make a cross-reference in the manuscript to page numbers and lines as done on

Page 24, lines 11-12.

• I do not approve to the term "free flame enthalpy" on Page 27, line 38.

Detailed Comments

In the following, I have tried to classify my comments into groups without any priorities; more a reflection of the sequence of reading the paper. Many of the comments refer to page numbers and line numbers printed in the left margin.

1. Unnecessarily difficult language with rather strange terms

There are a number of words/terms in the paper that are rarely found in scientific writing,

some are of an oral rather than written form and quite a few appears to be the result of using Google translate (or other systems) to convert non-English words into English. Some of these are listed in the following, in some cases with suggestions for alternative words:

• Even the title is somewhat hard to interpret. The word *primacy* means some kind of ranking, and the word *dissymmetry* refers to something that is not symmetric, whatever that means in the field of Thermodynamics. My interpretation of the title would then be that the concept of dissymmetry (somewhat unclear to me) is more important than the concept of *free energy*. Also, is "free energy" the same as *Gibbs free energy*?

• The concept of *exergy* is becoming increasingly important in academia, industry and funding agencies. This is formulated by the organization Science Europe as: "In a Resource-constrained world: Think Exergy, not Energy". I would recommend the author already in the abstract line 1 to change the text to "(i.e. available energy or exergy").

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• The word *purview* in the Abstract (".. the driving force to cause a system's change is the purview of the second law"). My dictionary indicates that the word means something like "area" or "field", and this does not help me to understand the sentence.

• The word *undergirded* used in the Abstract is not found in my dictionary. The author should consider finding a more descriptive word.

• The word *erected* in the Highlights could be replaced by "built on" or "based on".

• The word *explicates* in the Highlights actually means "explains", and I do not see any reason to use a more complicated word when you want to explain something. The same word is also used on Page 13, line 16.

• The word *consecrate* in line 28 of Page 1 is very rarely used. Better alternatives are "assign" or "nominate".

• The word *tread* (or its similar word *thread*) should be changed to something more appropriate in line 21 of Page 2.

• I am not sure I understand what is meant by*mature* second law in line 32 of Page 2.

• The term *entropy pessimism* in line 26 of Page 2 is strange in a scientific paper.

• The word *treatise* is used on Page 3, line 36, and is also in the title of reference (7) of the same author. This is an extremely rare word that actually (if I am right) means "thesis" or "dissertation".

• The word *supplants* used on Page 9, line 7 could be replaced by "displaces" or "replaces".

• The author uses several citations to quite old papers, and as a result, some rather strange words are encountered. One example is the word*annihilate* on Page 10, line 27, another is *hiatus* on Page 11, line 16. The latter is not even in my dictionary.

• On Page 11, the paragraph that starts with "Even with his intuition", there are two words that make it difficult to grasp the understanding of the text:*transcend* and *inexorability*.

• The word *epistemological* on Page 20, line 39, appears to be unnecessarily complicated.

• The word *presupposition* (used together with "epistemological") could be changed to "prerequisite," which is a much more common word.

• On Page 21, lines 30-31: I have tried my best, but I have to admit that I am not able to grasp the meaning of the phrase "the premise of primacy of energy over dissymmetry".

• On Page 21, line 41, the phrase "equation of motion for thermodynamic systems" is used. What kind of "motion" is this? In Engineering Thermodynamics, we most often neglect changes in kinetic (and potential) energy, so the only "motion" we have is fluids flowing in/out of our systems.

• The word *surmise* on Page 22, line 5, could be replaced by the more commonly understood word "assume". In the same sentence, the phrase "orthodox engineering thermodynamics" is used. I thought "orthodox" is related to religion, not engineering. Should "orthodox" be changed to "classical"?

• The word *demarcation* on Page 26, line 10, appears not to be the proper word in this context.

• The word *sans* on Page 27, line 9, does not make sense.

• The word *prodigious* in my dictionary means "fantastic," which is not a proper word in this context. The word "prodigious" should be replaced by something more appropriate. This word is also used on Page 31, line 24.

• In fact, the text on Page 28, lines 36-39 appears to more like a religious/social than scientific text with words like "mistakenly", "pessimistic", "fate", "indoctrinated", "myth", and the word/name "Anthropocene" is completely unknown to me.

• The word *bedrock* on Page 29, line 40, is easily understood, but rather concrete in this context. Would not "basis" or "foundation" be better?

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• The word *transmutes* on Page 29, line 40 actually means "transforms", which is a much easier word for the reader.

• The word *deceptive* on Page 30, line 4, could be replaced by the simpler "misleading".

2. Thermodynamic terms used in the paper

Unfortunately, the field of Thermodynamics has been known for its lack of standardization where different terms as well as mathematical symbols are used for the same thing:

• Free energy versus Available energy (line 1 of abstract).

• Available energy versus Exergy (on page 30, free energy is equalized with exergy).

3. Thermodynamic errors in the paper

As mentioned in the General Comments section, the most important error in the paper is the statement that Equation (8) only holds under quasi-staticity. This is surprising for such an experienced author in the field of thermodynamics. True, I need to use all my pedagogical skills to convince my students that this equation always holds. The complete story is the following:

• Thermodynamic work can only be related to volume change for internally reversible processes: = · .

• Heat can only be related to entropy change for internally reversible processes: = · .

• A "Property" in Thermodynamics is an entity that only depends on the state, not the process or path leading to that state. For pVT systems, state variables are p, V and T, while state functions (for closed systems) are internal energy U and entropy S.

• The 1st Law of Thermodynamics for a closed system is expressed by the following relation: = – , where the sign convention of Mechanical Engineering (i.e. heat transferred to the system is positive, while work produced by the system is also positive).

• The reason for using symbol for heat (Q) and work (W) is to indicate that these energies are not properties, since they do depend on the process/path to the current state.

• When introducing the expressions for work and heat above into the 1st Law of Thermodynamics, the resulting relation is obtained: = – . This is by many referred to as the Fundamental Property Relation.

• The surprising fact is that despite assuming internal reversible processes to obtain expressions for work and heat, once they are inserted into the 1st Law, the resulting expression holds for any process, whether reversible or irreversible. One way to argue for its general validity is that the relation only contains thermodynamic properties that

are independent of the process/path. A more pragmatic argument is that if this relation does not always hold, then the entire thermodynamic theory for pVT systems would break down.

Page 1, lines 16-17: The phrase "mechanical energy and available energy is wrong since *available energy* can be both mechanical energy (*work*) and thermal energy (*heat*). On this basis, I would suggest changing "dissipation of mechanical energy" in line 19 of Page 1 to "dissipation of exergy (i.e., the ability to produce work is reduced)".

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Page 4, line 39: The validity of Equations (8), (9), (10), and (11) is said to hold only for quasi staticity. I disagree; these equations always hold, refer to the discussion above.

Page 5, Equation (14): The "isolated material system" must also be "rigid" so that the total volume is constant.

Page 18, lines 28 and 29: Here, enthalpy is used for an isolated system, while it would be more correct to use internal energy. There are no material flows entering or leaving the system, thus, the pV part of enthalpy is zero.

The example illustrated by Figures 6 and 7 has the limitation that some of the details are "hidden" in the reference. There also seems to be an error in this example. For the temperature of the two blocks after the isentropic process, I got 217.3ºC, while the figure indicates 249.20ºC. Please check the calculations.

On Page 26, Equation (37), parentheses are missing before and after the Q/T terms.

4. Language Issues

The following are a few examples of language errors just as an indication or illustration and very far from being a complete list:

a) Abstract, line 3 from the end: Add "the" before "dissymmetry".

b) Highlights, line 1 of 1st bullet: Singular form "application" should be used.

c) Page 1, line 14: Add "the" between "heat" and "work".

d) Page 2, line 36: The word "necessity" must be changed to either "necessary" or "a necessity".

e) Page 3, line 18: The word "to" should be changed to "by".

f) Page 4, lines 7-8: The phrase "internal reversibility work and heat" should be changed to "internally reversible heat and work".

g) Page 5, line 1: Should not "or" be "for"?

h) Page 5, line 27: Add "an" before "isolated composite system".

i) Page 6, line 17: Should not "of" be "as" before "maximum entropy"?

j) Page 11, line 5: Here, "he's" should be replaced by "his".

k) Page 13, line 29: The word *momentous* before "significance" is a kind of "double up". When translating "momentous" to my own language and then translating back to English, I get the word "significant". Of course, the phrase "significant significance" does not make sense.

l) Page 14, line 17: The word "inputted" is not good language and should be replaced. One possible reformulation is "can be transferred into the Carnot Cycle".

m) Page 19, line 1: The following text is incomplete and poor language: "We assume a specific such a composite system".

n) Page 26, line 1: What is meant by "train" in the phrase "We train on the role of heat reservoir"?

o) Page 29, lines 12-15: The text here is highly confusing. First, the term "supreme" is used, and then in parentheses, the term "falsified" is used. This is rather confusing language that needs to be improved.

p) Page 29, lines 36-39: The sentence starting with "It is positive transformations" is

incomplete and leaves the word "possible" at the end with no link to the previous text.

q) Page 30, line 13: The phrase "That includes that" is poor language.

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r) Page 30, line 15: The text here is rather confusing: "unidirectional means processes

opposite to that of unidirectional is not possible".

s) Page 30, lines 22-23: Phrases such as "kill the goose" and "lays the golden eggs" are

not really scientific writing.

t) Page 31, line 7: In English, no sentence should start with "And".