

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

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**Potential competing interests:** No potential competing interests to declare.

This work will confuse readers because it is based on some profound misunderstandings.

It reviews many details of traditional thermodynamics,

but its GOAL is to argue that thermodynamics should be CHANGED.

Its BIG claim is that the concept of free energy is inadequate and should be replaced by "dissymmetry." Hence, let me ignore the parts that review basic problems in thermodynamics and concentrate on the problems with the parts of the paper that justify this BIG claim.

## (1) ERROR IN INTERPRETING WHAT MANY TEXTBOOKS SAY:

The author justifies the title of this paper by saying that

"The thesis of the paper is that the dissymmetry proposition of equilibrium thermodynamics—the second law of thermodynamics and its direct inference ... the maximization of total entropy—should be generalized to be the foundation (to be referred to as the dissymmetry premise) of the WHOLE thermodynamics." (page 2)

The problem is that most textbooks on thermodynamics ALREADY DO THIS.

Good textbooks give the second law of thermodynamics in terms of an increase in total entropy. The only thing this paper seems to do differently from those textbooks

is to use the term "dissymmetry" to refer to the "second law of thermodynamics." If I replace the words "dissymmetry proposition" with the words "second law" throughout this paper, then I see no fundamental difference from any good textbook (except for some confusions/errors mentioned below).

## (2) CENGEL AND BOLES (2008) IS POOR IN THIS REGARD, BUT OTHER BOOKS ARE BETTER.

I looked at the only engineering thermodynamics book cited in the paper, which is Cengel and Boles' "Thermodynamics: An Engineering Approach" (2008).

Indeed, it DOES use an OUTDATED definition of the second law of thermodynamics in its introduction (in section 1-1), saying it is related to a dissipation of energy. However, the modern definition of the second law in terms of entropy (which

is now more than 100 years old) is then given in chapter 7. So a reader who reads the whole book will get the right idea, but an unfortunate reader who only reads the introduction will be misled.

Given Cengel and Boles' poor presentation of the second law, I wanted to see how others did it. I am a physicist, and I did not know how engineering textbooks usually present the second law. So I googled for books on "engineering thermodynamics" and looked at the first three for which I found relevant snippets online:

(1) Balzhiser & Samuels, "Engineering Thermodynamics" (1977)

(1) Winterbone and Turan, "Advanced Thermodynamics for Engineers" (2015)

(2) Claire Yu Yan, "Introduction to Engineering Thermodynamics" (2022)

As far as I can tell from the parts that I could read online,

all of them define the second law in the correct way (the definition in terms of entropy).

So it seems the author of this paper has seen the poor presentation

of the second law in the introduction of Cengel & Boles' book and mistakenly thought that it was a universal problem in engineering thermodynamics books. It is not!

If other books have made the same mistake as Cengel and Boles, it would be helpful to the community if the author writes a paper pointing this out, but that paper MUST be concrete. It MUST name the books that get it wrong (and those that get it right), citing

the sections that get it wrong (or right), and explain how each one gets it wrong (or right).

## (2) ERROR IN INTERPRETING PLANCK'S STATEMENTS (WRITTEN 120 YEARS AGO):

The author thinks that the claim that free energy is inadequate is important enough to put in the paper's title, but this is based on a MISUNDERSTANDING.

The criticism of free energy is in section 4 and is based on a misunderstanding of Planck's statement made in 1903 when the laws of thermodynamics had only just been fully understood. Planck is cited as having written:

"The real meaning of the second law has frequently been looked for in a dissipation of energy... [But] there are irreversible processes in which the final and initial states show exactly the same form of energy ... They occur only for the reason that they lead to an appreciable increase of the entropy."

Thus Planck is warning readers that the second law is a law about entropy, not energy.

This was new to many readers 120 YEARS AGO, but it has long been integrated into all good books on thermodynamics, and has been a lesson well-learned by all students of thermodynamics for at least the last 100 years. More importantly, the "energy" that Planck is referring to here is "internal energy," not "free energy". So this cannot be a criticism of free energy.

Indeed, Planck's example sounds like a case where the Helmholtz free energy could explain the physics; an increase in entropy  $S$  for fixed internal energy  $U$  corresponds to a decrease in the Helmholtz free energy, since it is  $U-TS$ . So it is consistent with the usual application of free energy.

However, one should never forget that this free energy is derived from the laws of thermodynamics under the CONDITION that the system of interest is coupled to an infinite thermal bath at temperature  $T$  (as explained in any good book on thermodynamics). So, unlike the 1st and 2nd laws of thermodynamics, free energy is not meaningful for systems that do not fulfill this condition.

When the author concludes section 4 with

"In a nutshell, universal dissipation of free energy as a law of nature is not tenable."

His conclusion is not justified by anything written earlier in that section.

The arguments of Planck that he cites criticize the use of "energy," not "free energy".

At the same time, no one claims that free energy is a "law of nature".

The laws of nature are the first and second laws of thermodynamics, from which one derives free energy (under suitable conditions) in the manner ALREADY WELL EXPLAINED in any good book on thermodynamics written since 1903. If one is studying a situation that obeys these conditions (typically the system of interest being in thermal contact with a very large thermal bath at temperature  $T$ ), then free energy calculations work very well.

Note: Planck's book was written about 1897 and published in English for the first time in 1903

(<https://archive.org/details/treatiseonthermo00planuoft/>).

This is important because the explanation of thermodynamics given in that book was NEW to most readers in 1897, but it was rapidly accepted by the whole community and fully integrated into most thermodynamics books in the 20th century, including those for engineers.