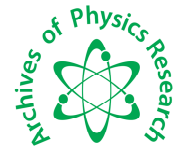




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Entropy: A concept that is not a physical quantity

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ABSTRACT

This study demonstrates that "entropy" is not a physical quantity, i.e., there is no physical quantity called "entropy". When heat engine efficiency is defined as: $\eta=W/W_1$, and the reversible cycles is decided to be Stirling cycle, if $\oint dQ/T=0$ is established, we can prove $\oint dW/T=0$ and $\oint dE/T=0$. If considering $\oint dQ/T=0$, $\oint dW/T=0$ and $\oint dE/T=0$ have defined new system state variables, It would be ridiculous to show such a definition. The fundamental error of "entropy" is that the polytropic process function Q is not a single-valued function of T in any reversible process, P - V figure should be P - V - T figure, so $\Sigma[(\Delta Q)/T]$ becoming $\int dQ/T$ is untenable. As a result, $\oint dQ/T=0$, $\oint dW/T=0$ and $\oint dE/T=0$ are all untenable, namely, there is not such formula as $\oint dQ/T=0$, $\oint dW/T=0$ and $\oint dE/T=0$ at all. Since the "absolute entropy" of Boltzmann is used to explain Clausius' "entropy" and the unit (J/K) of Boltzmann's "entropy" is also transplanted from the Clausius' "entropy", it is at the same time denied.

Key words: Physics, entropy, thermodynamics, statistical physics

INTRODUCTION

What is "entropy" ? This is a controversial question debated for more than 100 years.

Historically, based on the results obtained from the reversible cycle of any thermodynamics system that $\oint dQ/T = 0$, Clausius put forward a conclusion that there is a new system state variable in 1865: "Entropy" (indicated by the symbol S), and considered that "entropy" difference for any two equilibrium states in a system is:

$$\Delta S = S_2 - S_1 = \int_1^2 dQ/T$$

And thermodynamics can only calculate the difference. A well-known "entropy" increment law was put forward accordingly.

In 1872, Boltzmann put forward an absolute "entropy" formula, $S = k \ln \Omega$, where k is the Boltzmann constant, Ω is the thermodynamic probability, and "entropy" is considered as the degree of system confusion, or the measure marks of "order". This is considered as the best interpretation of "entropy", and people still use this interpretation today.

The above conclusions are still be widely accepted and learned. We can find the above content in any textbooks of thermodynamics and statistical physics. "Entropy" has been widely used as an important physical quantity although we are not certain what "entropy" really is.

There are many unresolved problems or conflicts which are difficult to justify in above conclusions, which indicates that "entropy" is problematic.

II "Entropy" is not a physical quantity

§ 2.1 The origin of "Entropy"

To illustrate "entropy" is not a physical quantity, we should first review the origin of "entropy" briefly:

First, the heat engine efficiency is defined as $\eta = W/Q_1$, that is, taking the ratio of W to Q_1 as a heat engine efficiency, where W is the net work that the heat engine cycle generated to the external world and Q_1 is the heat the system absorbed from the outside; and, Carnot cycle $\eta = W/Q_1 = 1 - Q_2/Q_1$, η has nothing to do with the system working substance, and it only relates to the two constant temperature heat sources. Therefore, the definition of thermodynamics temperature scale is θ : $\theta_2/\theta_1 = Q_2/Q_1$. When the system working substance is ideal gas, we can prove that:

$$Q_2/Q_1 = T_2/T_1 \quad \text{that is} \quad \theta_2/\theta_1 = T_2/T_1$$

still use symbol T to show the thermodynamic temperature scale, i.e., $Q_2/Q_1 = T_2/T_1 \Rightarrow Q_1/T_1 + Q_2/T_2 = 0$, where Q_2 is the heat release and which is negative itself. Thus, for any reversible cycle, an infinite number of Carnot cycles is used to approximate and substitute arbitrary reversible cycles process, then then, get $\oint dQ/T = 0$, therefore, people believe that dQ/T is a complete differential and $\oint dQ/T = 0$ is used to determine a system status quantity, that is entropy.

§ 2.2 "Entropy" is not a physical quantity

"Entropy" came from $\oint dQ/T = 0$, therefore, if we want to prove that "entropy" is not a physical quantity, we only need to prove $\oint dQ/T = 0$ cannot define a physical quantity or itself is untenable.

We know $\oint dQ/T = 0$ is from the constant $Q_2/Q_1 = T_2/T_1$ in Carnot cycle, which is the method used to define the thermodynamic temperature scale. The basis of its existence lies in the combination of the definition of heat engine efficiency and the Carnot cycle. We should know that the heat engine efficiency formula is a definition, while the Carnot cycle is different from other reversible cycles just in forms, so it should not occupy a higher status than other forms of cycles, and the role of defining the thermodynamic temperature scale should not be unique.

Let us prove that $\oint dQ/T = 0$ cannot define physical quantity and itself is untenable as follows.

Above all, We redefine the heat engine efficiency.

The heat engine efficiency is only meaningful to the observer, how to define the efficiency of heat engine has nothing to do with the objective process of heat engine system. Therefore, we can use other means to define the heat engine efficiency in a reasonable way. Now the efficiency of heat is redefined as the ratio of the net work that the heat engine system has done to external world in a cycle to the work that the system has done to external world,

$$\eta = \frac{W}{W_1} \quad \dots\dots\dots (2.2.1)$$

That is, the work W_1 that the system has done to the external world in the cycle will take place of the heat Q_1 that the system has absorbed from the external world in the original definition of $\eta = W/Q_1$. Because the work W_1 that the system has done to the external world in the cycle cannot be totally transformed into the net work W , this is just like the heat that the system has absorbed from the external world in a cycle cannot become all the net work to the outside – according to the expression of Kelvin's second law, therefore, these two definitions have the same meaning. Here the second law can be given in another way: there can be no such engines, all its work done to external world in the cycle can be transformed into the net work done to the external world. Obviously, this expression is equivalent to the Kelvin expression.

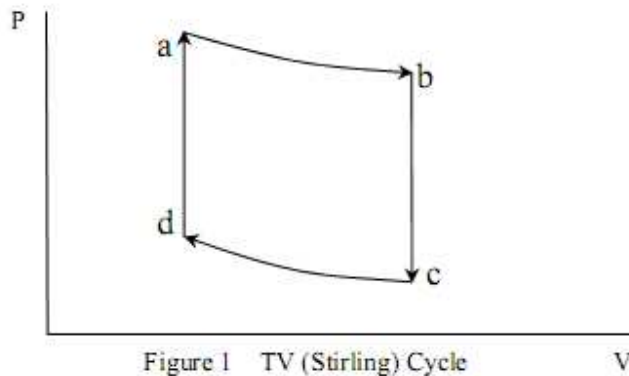
Now, there is a heat engine that uses a certain amount of working substance to do work W_1 to the external world in a cycle, and the external world will also do work W_2 to the system for system recovery. Thus,

$$W = W_1 - W_2$$

From (2.2.1) we can see:

$$\eta = \frac{W}{W_1} = 1 - \frac{W_2}{W_1} \dots\dots\dots(2.2.2)$$

Now take the Stirling reversible cycle shown in Figure 1 as the unit cycle and it plays the role of Carnot cycle during the process of eliciting $\oint dQ/T = 0$



abeda consists of two reversible isochoric processes (i.e. bc and da), and two reversible isothermal processes (i.e. ab and cd).

Here, we call the heat source that exchange energy power with system in the isothermal process as the work source in order to facilitate the understanding of the followings. Here the cycle is referred to as the TV cycle for short, and the heat engine doing TV cycle (namely Stirling cycle) is TV engine.

It is proven below that all reversible engines (i.e. TV engine) that only work between two constant temperature work sources have the same efficiency, and irreversible engines have lower efficiency than reversible engines.

Take two engines, E and E', E is reversible engine, E' is any engine, they both work between constant temperature work sources θ_1 and θ_2 , and they have arbitrary working substance. Use θ_1 and θ_2 to show the high temperature and low-temperature work sources respectively, $\theta_1 > \theta_2$, here θ could be any temperature scales. Assume that E and E' do the same net work to the external world in a cycle, i.e. ΔW_1 and ΔW_2 , and it is always $\Delta W_1 = \Delta W_2 = W$ (a situation similar to the Carnot cycle). Use W_1 and W_1' to show the work done by the E and E' in a cycle; W_2 and W_2' are the works that the external world has done to E and E', η and η' are the efficiencies of E and E'. Firstly we prove that $\eta' \leq \eta$ by contradiction,

Assume $\eta' > \eta$

Since E is invertible, so E can reverse movement. Then W_2 is the work that E has done to the external world, and W_1 is the work the external world has done to E, while W is the net work the

external world has done to E, and $W = W_1 - W_2$, W is provided by E' ; the heat $\Delta Q = W$ ($= \Delta W_1 = \Delta W_2$) that E' absorbed in the cycle is provided by E,

Therefore
$$\frac{W}{W_1'} > \frac{W}{W_1} \Rightarrow W_1 > W_1'$$

Also, because

$$W_2 = W_1 - W$$

$$W_2' = W_1' - W$$

Then
$$W_2 > W_2'$$

Assume that E' and E which run in reverse directions incorporated into a heat engine, after a combined cycle, the system will recover and the only result will be the system absorbs work $\Delta W = W_2 - W_2'$ from the low-temperature work source (i.e. heat source θ_2) and automatically does work $\Delta W = W_1 - W_1' = W_2 - W_2'$ to the high-temperature work source (i.e. heat source θ_1). That is, the heat equal to $\Delta W = W_1 - W_1' = W_2 - W_2'$ is sent from the low-temperature work source (i.e. heat source θ_2) to the high-temperature work source (i.e. heat source θ_1) automatically. This is directly in contradiction with the expression of the second law of Clausius, that is, $\eta' > \eta$ is untenable, thus, there must be:

$$\eta' \leq \eta \dots\dots\dots (2.2.3)$$

If E' is also reversible engine, Similarly, take the E' engines to run in the reverse direction, it is proved that $\eta > \eta'$ is untenable. That is, if E and E' are both invertible, then, $\eta > \eta'$ and $\eta' > \eta$ are both untenable, thus, there must be:

$$\eta = \eta' \dots\dots\dots (2.2.4)$$

If E' is an irreversible engine, i.e., it is not a TV engine, then the equal mark in $\eta' \leq \eta$ cannot hold, according to the usual method of proof in Carnot cycle situation, because if $\eta = \eta'$, obviously after the combined cycle of E which runs in reverse direction and E', the system and the external world will complete recover, then E' can only be a reversible engine, this is contradictory to the fact that E' is a reversible engine, thus, if E' is not a reversible engine, there must be

$$\eta' < \eta \dots\dots\dots (2.2.5)$$

In this way, we can prove that under the definition of (2.2.1), all reversible engines (i.e. TV engine) that only work between two constant temperature work sources have the same efficiency; the efficiency of irreversible engine is less than the efficiency of reversible engine, has nothing to do with the working substance .

As the efficiency of TV engine has nothing to do with working substance, the thermodynamics temperature scale (absolute thermometric scale) can be defined as

$$\frac{\theta_1}{\theta_2} = \frac{W_1}{W_2} \dots\dots\dots (2.2.6)$$

That is to say that the ratio of two thermodynamic temperatures is the ratio of the work W_1 done by the TV engine that work between the two temperature work sources(namely, heat source) and the work W_2 that the outside did to the TV engine.

When the working substance is ideal gas, and the system do TV cycle, then,

$$\eta = 1 - \frac{W_2}{W_1} = 1 - \frac{\int_{V_2}^{V_1} PdV}{\int_{V_2}^{V_1} P' dV'} = 1 - \frac{\nu RT_2 \ln \frac{V_2}{V_1}}{\nu RT_1 \ln \frac{V_2}{V_1}} = 1 - \frac{T_2}{T_1} \dots\dots\dots (2.2.7)$$

Comparing (2.2.6) and (2.2.7), we know, to the ideal gas $\theta_2 / \theta_1 = T_2 / T_1$, that is, the thermodynamic temperature scale which is defined by (2.2.6) is equivalent to the thermodynamic temperature scale which is defined by $\theta_2 / \theta_1 = Q_2 / Q_1$. Habitually, we still use the symbol T to represent the thermodynamic temperature scale as follows,

$$\frac{T_1}{T_2} = \frac{W_1}{W_2} \dots\dots\dots (2.2.8)$$

It can be deduced from (2.2.8) that

$$\frac{W_1}{T_1} + \frac{W_2}{T_2} = 0 \dots\dots\dots (2.2.9)$$

W_2 is the work that the external world has done to the system and it is negative. It is exactly the same with the process of deducing $\oint dQ/T = 0$, using a serial element TV cycles to split and replace any reversible cycles of the system, as shown in Figure 2,

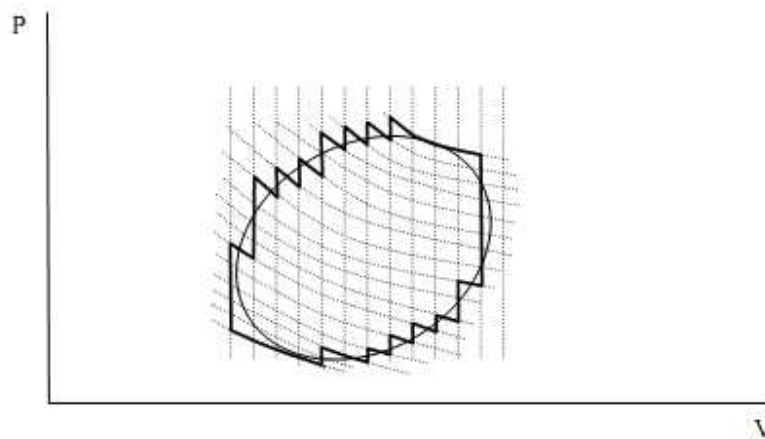


Figure 2 A Series of TV Cycles Split and Replace Any Reversible Cycle

On the two isochoric processes of TV cycle, there is always $\Delta W=0$, i.e. $dW=0$, so when the number of element processes is infinite, namely, while systems and infinite work sources (i.e. heat sources) exchanging work (equivalent to the heat), there occurs

$$\oint \frac{dW}{T} = 0 \quad \dots\dots\dots (2.2.10)$$

Again, this result has nothing to do with the working substance of the system.

Obviously, as for the irreversible cycle, we can deduce the conclusion: $\oint \frac{dW}{T} < 0$

At this point, we get a conclusion that $\oint dW/T = 0$, which is paratactic with $\oint dQ/T = 0$. Then according to the first law $dE = dQ + dW$, we can also get, for any reversible cycle of thermodynamic system, there is

$$\oint \frac{dE}{T} = \oint \frac{dQ}{T} + \oint \frac{dW}{T} = 0$$

Over the past hundred years, people think that $\oint dQ/T = 0$ defines a system state variable, namely, "entropy". Then we can deduce that

$$\oint \frac{dW}{T} = 0 \quad \text{And} \quad \oint \frac{dE}{T} = 0$$

inevitably defines new system state variables. In the reversible adiabatic process for example, while the system reaches another different equilibrium state 2 from equilibrium state 1:

$$\int_1^2 \frac{dQ}{T} \neq \int_1^2 \frac{dW}{T} \quad \dots\dots\dots (2.2.11)$$

$$\int_1^2 \frac{dQ}{T} \neq \int_1^2 \frac{dE}{T} \quad \dots\dots\dots (2.2.12)$$

during the system reversible isochoric process, for different equilibrium states 3 and 4, there is

$$\int_3^4 \frac{dW}{T} \neq \int_3^4 \frac{dE}{T} \dots\dots\dots (2.2.13)$$

According to (2.2.11) ~ (2.2.13), we can know that if $\oint \frac{dQ}{T} = 0$, $\oint \frac{dW}{T} = 0$ and $\oint \frac{dE}{T} = 0$ define new system state variables, then they are different from each other and their dimensions are the same, i.e. J/K . Therefore the system has only one state variable, but various values; or the system has three different state variables in the same unit. Although different state variables with the same unit can exist in one system, but we have already no idea about one S, thus obviously this should be ridiculous now to have to "define" three.

Thus, the conclusion is: $\oint \frac{dQ}{T} = 0$ cannot define physical quantities.

Similarly, $\oint \frac{dW}{T} = 0$ and $\oint \frac{dE}{T} = 0$ cannot define physical quantity either.

III $\oint dQ/T = 0$ is a wrong formula based on a wrong calculus deducing

So, what is $\oint dQ/T = 0$?

In the textbooks, it is emphasized that $\oint dQ/T = 0$ is a physical result rather than a mathematical conclusion. That is, $\oint dQ/T = 0$ can not be obtained by mathematical derivation. If there is this result of $\oint dQ/T = 0$, then it must define a system state variable, and this study has already demonstrated the absurdity that $\oint dQ/T = 0$ could define the physical quantities. This means that this conclusion $\oint dQ/T = 0$ is untenable.

The key error of "Entropy" is that we cannot deduce this mathematical conclusion $\oint dQ/T = 0$ from physics, that is, the conclusion of $\oint dQ/T = 0$ is untenable. The key question is, in the process of deducing the relational expression of $\oint dQ/T = 0$, $\Delta Q/T \rightarrow dQ/T$ is taken for granted in the process $\sum[(\Delta Q)/T]$ becoming $\int dQ/T$ is false.

Because:

- 1、 The prerequisite for the establishment of differential is the existence of differentiable function. Here we need to change $\Delta Q/T$ into dQ/T on the premise of the existence of a differentiable function $Q=f(T)$, but there is no corresponding differentiable function here.
- 2、 As for the element calculus, we know that element calculus is the application of calculus under the premise of the existence of differentiable function.

3、As for the element calculus, when Q is a function, assume Q is a single-valued function of T , i.e. $Q=f(T)$, then it can be deduced that $1/TdQ=dF(T)$ and $\int_T 1/TdQ=\int_T dF(T)$. In this case, $\Delta Q/T \rightarrow dQ/T$ is tenable.

However, we know that for any reversible process, Q is not a single-valued function of T , but $Q=f(T,V,P)$, here, between two different states, $Q=f(T,V,P)$ has innumerable forms, it is process quantity depending on path, but to given path reversible process, the form of $Q=f(T,V,P)$ is unique. So, $1/TdQ=dF(T,V,P)$. For any reversible process, generally speaking, P , V and T are all variables, in fact, P-V figure should be P-V-T figure, in P-V-T figure it is clear that only $\int_T \int_V \int_P 1/TdQ=\int_T \int_V \int_P dF(T,V,P)$ is meaningful, in P-V-T figure, it is also clear that a series of Carnot cycles splitting and replacing any reversible cycle in P-V figure is absurd at all, for example, reversible adiabatic process could be reversible adiabatic cycle, to reversible adiabatic cycle, Carnot cycles splitting and replacing it is untenable, the so called process of ΔQ (in reversible isothermal processes) replacing dQ (in any reversible process) is untenable at all either, and so on. What does $\int_T 1/TdQ=\int_T dF(T,V,P)$ mean? Obviously, it is meaningless. This is meaningful only to three variables (generally speaking, two of the three variables are independent variable.) integral, but it is meaningless to the formula of one variable integral. dQ/T (i.e. $df(T,V,P)/T$) itself is meaningless.

Therefore, $\Delta Q/T \rightarrow dQ/T$ is the misuse of the element calculus, and the essence of dQ/T (or say, as some people like, $\delta Q/T$) is $df(T,V,P)/T$, but this is meaningless. People do not follow the principles of calculus, resulting in the illusion that the variable ΔQ which only plays a role of quantity in the Carnot cycle reversible isothermal process and the polytropic process function $Q=f(T,V,P)$ in any reversible process have the same nature, as a result, people took $\Delta Q/T \rightarrow dQ/T$ for granted.

CONCLUSION

" $\oint dQ/T = 0$ " is neither a mathematical conclusion nor a physical result, the formula $\oint dQ/T = 0$ is untenable, similarly, $\oint dW/T = 0$ and $\oint dE/T = 0$ are untenable either. There is no so-called physical quantity as "entropy".

IV About Boltzmann's "entropy"

So, what is Boltzmann's "entropy"? Boltzmann's "entropy" is used to explain the Clausius' "entropy" and the unit (J/K) of Boltzmann's "entropy" is also taken from the Clausius' "entropy", for Boltzmann's "entropy" $S = k \ln \Omega$ is the artificial combination of a purely digital $\ln \Omega$ and Boltzman constant k which has unit (J/K), this formula is a man-made formula. This study has demonstrated that the Clausius "entropy" does not exist, and then the Boltzmann "entropy" is denied at the same time.

It is impossible to try to deduce "entropy" in statistical physics directly. On one hand, it also has to go through a key step that translates infinitesimal into differential, but as the above mentioned, this step is untenable; on the other hand, the units (J/K) of statistical physics "entropy" (Boltzmann's "entropy") are transplanted from Clausius' "entropy", so if Clausius' "entropy" does not exist, there would be no the transplant source of the unit (J/K) of Clausius' "entropy". As a result, statistical physics "entropy" is left with only a pure digital, and there is no physical meaning.

In addition, even if we do not consider the issue of the unit, from a pure probability point of view, in the $S=k\ln\Omega$, Ω is the so-called thermodynamic probability, and the calculation of Ω should use the phase cell division in surpassing space μ . The phase cell is $2i$ -dimensional, i is the total degree of freedom of the molecule within the system. The essence of calculating Ω is the discretization of the continuous μ space, and giving it an objective meaning. In fact, this approach does not work, regardless of how much work people have done so far, there will be no objective conclusion, the reason being that there is no objective and with physical meaning criteria for the division phase cells, that is, Ω has no objective meaning in physics. Afterwards in light of Combine Liouville theorem and the conclusions of this paper, Boltzmann's "entropy" can be seen as a technique for displaying irreversibility from a purely probabilistic point of view.

V About the second law of thermodynamics

The second law of thermodynamics is expressed by several equivalent statements. Although they have been proved by numerous facts, we can not conceal the fact that they are the phenomenological laws. Just as we express the law of gravity as: any object can not move from the lower place to high place spontaneously, the various expressions of the second law are statements of specific phenomena, which fails to reveal the unified and essential law of resulting in these phenomena. The second law of thermodynamics will be re-described by a new method.

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