Entropy - A concept that is not physical quantity

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Abstract: The author demonstrated that entropy is not a physical quantity.

Though proof by contradiction, we know, in any reversible cycle of arbitrary thermodynamics system, the conclusion $\oint dQ/T=0$ does not means there is a new system state variable, in fact, the formula $\oint dQ/T=0$ itself is untenable. Second law of thermodynamics is correct, but entropy is nothing. Correspondingly, we can know the nature of Boltzemm statistical entropy. For there is not such system state variable as entropy, so, the second law of thermodynamics has to be rebuilt.

Key words: entropy, thermodynamics, state variable

1. Introduction

What is entropy?

This is a problem that has been arguing for more than one hundred years.

In history, in 1865, based on the conclusion $\oint dQ/T=0$ in any thermodynamic system reversible cycle, Clausius advanced that there was a new system state variable——Entropy for the first time, and he thought the entropy difference between any two equilibrium states of any thermodynamic system is $\triangle S=S_2-S_1=\int_1^2 dQ/T$, where S expresses entropy, and in thermodynamics, only the entropy difference could be calculated. Correspondingly, the principle of entropy increase was put forward.

Subsequently, in 1872, basing on statistical method, Boltzemm advanced the formula of absolute entropy $S=k\ln\Omega$, k is boltzemm constant, Ω is thermodynamic probability, and he thought that entropy was a quantity to measure the order of a system, this was regarded as the best explanation on entropy, up to now, people still adopt this explanation.

The abovementioned conclusions are still learned extensively in the world, they can be found in any text book of thermodynamics or statistical physics. Entropy has been regarded as an important physical quantity and extensively used, although people can't determine what entropy is on earth.

As we know, there are also many important problems and contradictions on entropy that can't be solved up to now, this indicates there must be something wrong with entropy.

2. Entropy is not a physical quantity

§2.1 The origin of entropy

In order to expound the conclusion that entropy is not a physical quantity, above all , let's chiefly review the origin of entropy.

Firstly, to define heat engine efficiency as $\eta=W/Q_1$,where w is the net work the heat engine applied to the outside in one cycle, Q_1 the heat quantity the heat engine absorbed from the outside in this cycle, so to Carnot cycle, $\eta=W/Q_1=1-Q_2/Q_1$, that is, η is only decided by the two values of heat quantity Q_1 the system absorbed from the high temperature heat source and heat quantity Q_2 the system released to the low temperature heat source in the Cycle. η has nothing to do with system working medium, so, thermodynamics temperature scale θ was defined as $\theta_2/\theta_1=Q_2/Q_1$, when the working medium was ideal gas, it was proved there was $Q_2/Q_1=T_2/T_1$, namely, $\theta_2/\theta_1=T_2/T_1$, still let T express thermodynamic temperature scale, then, $Q_2/Q_1=T_2/T_1 \Rightarrow Q_1/T_1+Q_2/T_2=0$, where Q_2 is the heat quantity the system released to the low temperature heat source, it is negative in $Q_1/T_1+Q_2/T_2=0$. Via the process we all know, to arbitrary reversible cycle of any thermodynamic system, $\oint dQ/T=0$ was obtained. Basing on this conclusion, people regard dQ/Tas a perfect differential, and thought that $\oint dQ/T=0$ determined a new system state variable——entropy.

§2.2 Proof of entropy being not a physical quantity

In essence, entropy stemmed from the formula $\oint dQ/T=0$, so, to prove entropy is not a physical quantity, we must and only need to prove $\oint dQ/T=0$ can not determine physical quantity at all.

We know, the essential prerequisite of $\oint dQ/T=0$ is that there always is $Q_2/Q_1=T_2/T_1$ in Carnot cycle, while the formula $Q_2/Q_1=T_2/T_1$ is the way to define thermodynamic temperature scale, and it's premises are heat engine efficiency formula and Carnot cycle, but heat engine efficiency formula is only a definition formula, moreover, there are not essential distinctions between Carnot cycle and other reversible cycle, the function that Carnot cycle can be used to define thermodynamics temperature scale should not be unique. Now, let's prove that $\oint dQ/T=0$ can not determine physical quantity :

Firstly, to define heat engine efficiency anew.

Because the heat engine efficiency is a definition, just as the way people adopted in history $\eta=W/Q_1$, we can also reasonably define it by other way. Now we anew define heat engine efficiency η as:

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

that is, replacing Q_1 in the original definition $\eta=W/Q_1$ with W_1, W still is the net work the heat engine applied to the outside in one cycle. Obviously, W_1 can not be completely delivered to W, in fact, only when the system temperature could reach absolute zero, the work the outside applied to the system in a cycle could be zero, then W can be completely delivered to W_1, but, it is well known, absolute zero can not be reached—third law of thermodynamics, namely, in a cycle, there inevitably is $W < W_1$. So, the definition (2.2.1) is meaningful just as the original definition $\eta=W/Q_1$.

Accordingly, another expression of second law of thermodynamics can be put forward**:** it is impossible to make such heat engine that **the work** it applies to the outside in a cycle completely delivered into **the net work** it applies to the outside.

Now, there is a heat engine, in a cycle, a determined amount of working medium applied work W_1 to the outside, the outside applied work W_2 to the heat engine system, then the system restored its initial state, so, $W=W_1-W_2$, then according to formula (2.2.1)**:**

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

let the reversible cycle **abcda** in fig.(2.2.1) be element cycle, it plays the part of Carnot cycle in the process

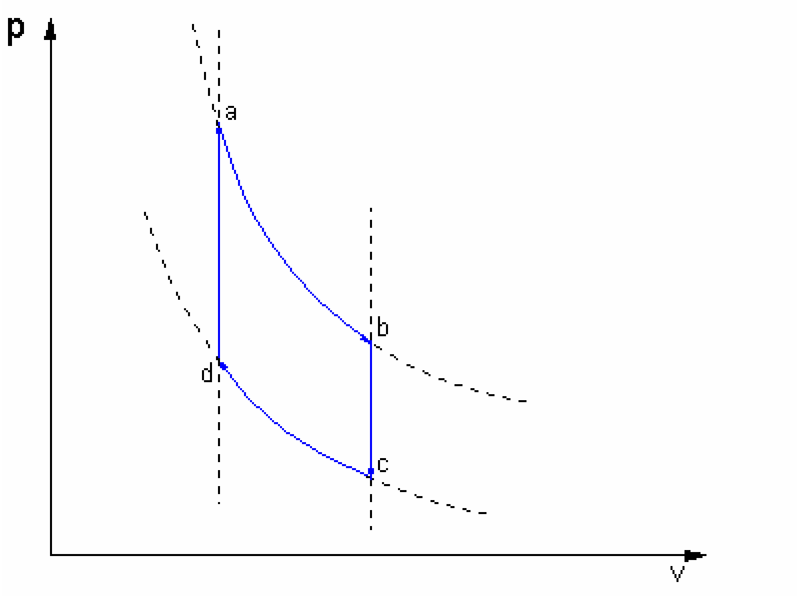

Fig 2.2.1

of deducing $\oint dQ/T = 0$. The reversible cycle abcda is composed of two isometric processes bc、da and two isothermal processes ab、cd.

In order to more easily understand the following content, the source that transformed energy with the system in isothermal process is named "work source" to replace the name "heat source", certainly, they are equivalent; and such cycle as **abcda** is named TV cycle for short, in TV cycle, there is no work delivering apart from the processes that relates with **work source**, such kind of heat engine that carries out TV cycle is named TV engine.

Now, to demonstrate this law: the efficiencies of all reversible heat engines that only work in the same two constant temperature work sources are equal, the efficiencies of irreversible heat engines are lower then that of reversible heat engines.

The proof is as follows:

Let E and E' be any two reversible heat engines, they both work between the same two constant temperature **work source** θ_1 and θ_2 , inevitably, both this two heat engines are TV engines, their work medium are arbitrary; to express the temperature of he high temperature work source θ_1 and the temperature of the low temperature work source θ_2 with θ_1 and θ_2, $\theta_2 > \theta_1$, here, θ is any kind of temperature scale. To regulate the working processes of this two TV engines, let E and E' apply work W_1 and $W_1^{/}$ to the outside when the temperature of E and E' is $\theta_{1,}$ the outside apply work W_2 and $W_2^{/}$ to E and $E^{/}$ when the temperature of E and $E^{/}$ is θ_2, $\triangle W_1 = W_1 - W_2$, $\triangle W_2 = W_1^{/} - W_2^{/}$, and let $\triangle W_1 = \triangle W_2 = W$, $\triangle W_1$ and $\triangle W_2$ are the net works E and $E^{/}$ apply respectively to the outside in the cycle, via regulating the working processes of this two TV engines, obviously, $\triangle W_1 = \triangle W_2 = W$ can always be realized.

Let η and η' be the efficiencies of the two heat engines E and $E^{/}$, above all, to prove

$$\eta = \eta'$$

through apagoge **:**

assuming $\eta' > \eta$

because both E and E' are reversible, let E run in the opposite direction, then E becomes a refrigerating engine, at this moment, E applies work W_2 to the outside, the outside world apply work W_1 to E, the net work the outside applies to E is $W=W_1-W_2$, let this work W be provided by E' that works in positive direction as a heat engine, and the heat $\triangle Q=W(=\triangle W_1=\triangle W_2)$ that E' absorbed in the cycle is provided by E, for

$$\eta' > \eta$$

then $$\frac{W}{W_1'} \rangle \frac{W}{W_1} \Rightarrow W_1 \rangle W_1'$$

here, although E is a refrigerating engine, but the efficiency we considered is heat engine efficiency, so $\eta=W/W_1$, where W_1 is the work the heat engine applies to the outside in the cycle, and there is:

$$W_2 = W_1 - W$$
$$W_2' = W_1' - W$$

so $W_2 > W_2'$

let E and E' that run in opposite direction combine into one heat engine, then, after the combined system of E and E' cycles one time, this system restores, the only result is the system absorbs heat from the low temperature work source θ_2 and applies work $\triangle W=W_2-W_2'$, and the work $\triangle W$ automaticly delivers into the $\triangle W=W_2-W_2' =W_1-W_1'$ that the outside world applies to the system when the temperature of the system is θ_2, that is the combined system restores after a cycle, the only result is:

there is heat $\triangle Q=\triangle W=W_2-W_2'=W_1-W_1'$ being delivered to the high temperature heat source(namely work source) θ_1 from the low temperature heat source (namely work source) θ_2 automaticly. This is directly in contradiction with Clausius expression of second law of thermodynamics, so, $\eta' > \eta$ is untenable.

Similarly, let E' run in opposite direction, then, via the abovementioned method, it can be proved that $\eta>\eta'$ is untenable, so, there must be:

$$\eta=\eta' \text{ ---------------(2.2.3)}$$

while, if E' is irreversible heat engine, as the abovementioned, it can be proved that $\eta' >\eta$ is untenable, on the other hand, because E' can not run in opposite direction, then, it can not be proved that $\eta>\eta'$ is untenable, so, we obtain:

$$\eta' \le \eta \text{----------------(2.2.4)}$$

however, there is already a reversible heat engine E', after the combined system cycles one time, both the system and the outside world restore, so, if E' is irreversible heat engine, then the equation in $\eta' \le \eta$ is untenable. Now , we obtained, if E' is irreversible heat engine, then:

$$\eta' < \eta \text{ ---------------(2.2.5)}$$

then, it is proved that the efficiencies of all reversible heat engines that only work in the same two constant temperature work sources(namely heat source) are equal, the efficiencies of irreversible heat engines are lower then that of reversible heat engines.

Since the efficiency of TV engine is unrelated with working medium, so, thermodynamics temperature scale θ can be defined as:

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

that is, the specific value of two thermodynamics temperature θ_1 and θ_2 is the specific value of W_1 and W_2 .

when working medium is ideal gas, and the cycle is TV cycle, to any heat engine that works with υ mol ideal gas,

$$\eta = 1 - \frac{W_2}{W_1} = 1 - \frac{-\int_{V_2}^{V_1} P'dV'}{\int_{V_1}^{V_2} PdV} = 1 - \frac{\int_{V_1}^{V_2} P'dV'}{\int_{V_1}^{V_2} PdV} = 1 - \frac{\upsilon R T_2 \ln\frac{V_2}{V_1}}{\upsilon R T_1 \ln\frac{V_2}{V_1}} = 1 - \frac{T_2}{T_1} \cdots\cdots\cdots\cdots (2.2.7)$$

compareing formula(2.2.7) with (2.2.6), to ideal gas, there is $\theta_2/\theta_1 = T_2/T_1$, so, obviously, this thermodynamics temperature scale defined by formula (2.2.6) is equal to that defined by $\theta_2/\theta_1 = Q_2/Q_1$ in history. From habit, still express thermodynamics temperature scale with the symble T, namely

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

via formula (2.2.8), there is

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

where, W_2 is the work the outside world applied to the heat engine system, its value is negative.

According to the same method as deducing $\oint dQ/T=0$, to cut and replace arbitrary reversible cycle of any thermodynamics system with a set of element TV cycle, see fig.2.2.2,

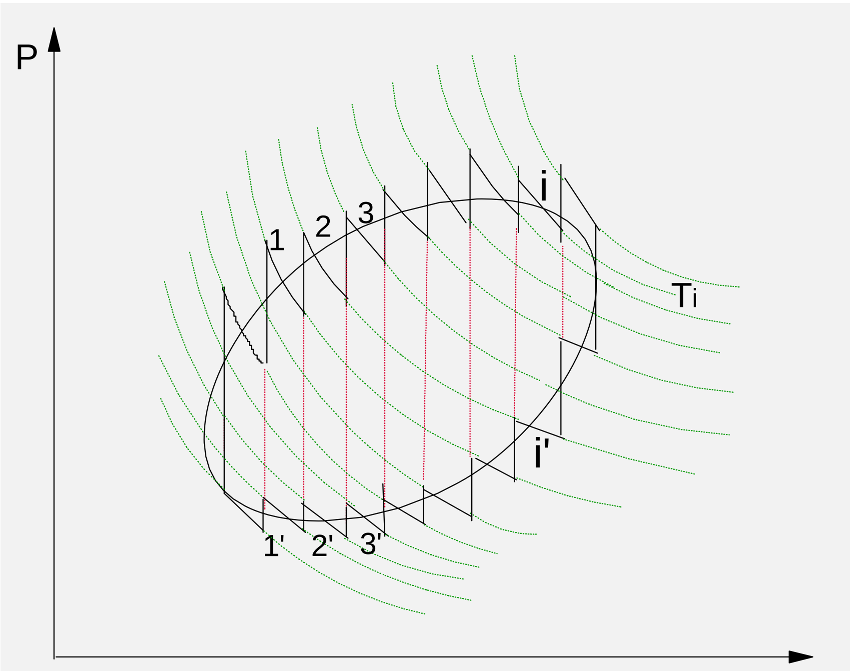

fig. 2.2.2

because there always is ΔW=0 in the two isochoric processes of any TV cycle, namely, dW=0, when the numberof element processes is infinite, namely, the heat engine system exchanges work with infinite work sources, there is

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

this result has nothing to do with working medium. Obviously,When cycle process is irreversible, it is easy to obtained $\oint \frac{dW}{T} < 0$, namely, to arbitrary thermodynamic system cycle, there is $\oint \frac{dW}{T} \leq 0$.

Up to now, we obtained the following conclusions on arbitrary thermodynamic system reversible cycle:

$$\oint \frac{dQ}{T} = 0 \qquad \oint \frac{dW}{T} = 0$$

relating to the first law of thermodynamics dE= d(Q+W), to arbitrary thermodynamic system reversible cycle,

$$\oint \frac{dE}{T} = \oint \frac{d(Q+W)}{T} = \oint \frac{dQ}{T} + \oint \frac{dW}{T} = 0 \cdots\cdots\cdots\cdots (2.2.11)$$

It is more then one handred years that people maintained ∮dQ/T=0 defined a new system state variable, namely the so called “ entropy ”, if so, according to such inference, it is inevitable that both ∮dQ/T=0 and ∮dE/T=0 also define new system state variables, just as dQ/T, dW/T and dE/T are also perfect differentials, let dQ/T=dS, dW/T=dR, dE/T=dK, then, for example, in system reversible adiabatic process, when the system reaches to equilibrium state 2 from a different equilibrium state 1, as we know T≠0, there is

$$dQ = 0 \Rightarrow dQ/T = 0 \Rightarrow \int_1^2 dS = 0$$

$$dW \neq 0 \Rightarrow dW/T \neq 0 \Rightarrow \int_1^2 dR \neq 0$$

$$dE \neq 0 \Rightarrow dE/T \neq 0 \Rightarrow \int_1^2 dK \neq 0$$

$$\Rightarrow \begin{array}{l} \int_1^2 dS \neq \int_1^2 dR \\ \int_1^2 dS \neq \int_1^2 dK \end{array} \qquad \text{-------}(2.2.12)$$

and in reversible isochoric process, to two different equilibrium states 3 and 4, there is

$$dW = 0 \Rightarrow dW/T = 0 \Rightarrow \int_3^4 dR = 0$$

$$dE \neq 0 \Rightarrow dE/T \neq 0 \Rightarrow \int_3^4 dK \neq 0$$

$$\Rightarrow \int_3^4 dR \neq \int_3^4 dK \qquad \text{------}\ (2.2.13)$$

if ∮dQ/T=0, ∮dW/T=0 and ∮dE/T=0 really define new system state variables, from formula (2.2.12) and (2.2.13) we know, the three state variables S, R and K are inevitably different from each other; on the other side, their dimensions are the same one, namely J/K, and they are all state variables. So, we have to "**make**" three different system state variables with same dimensions, and we don't know what they are, no doubt, this is absurd.

Up to now, the conclusion inevitably is: $\oint dQ/T=0$ does not define new system state variable, either don't $\oint dW/T=0$ and $\oint dE/T=0$.

§2.3 The truth of the problem

Since $\oint dQ/T=0$ does not means there is a new system state variable, what is the real situation?

In fact, there are not such formula as $\oint dQ/T=0$、$\oint dW/T=0$ or $\oint dE/T=0$ at all !

Why ?

As we know, in order to reach the conclusion $\oint dQ/T=0$, there is a key point that to replace ΔQ with dQ, and predecessors stated that this is a "physical conclusion".

But, replaceing ΔQ with dQ is taking for granted, if only we review the definition of differential, we know that the prerequisite of differential is there is a function $y=f(x)$, however,there is not any function as $Q=f(T)$ here at all, so, ΔQ can not become dQ. Besides this,there are other necessary conditions of differential being tenable that we all know, there is not any basis to replace ΔQ with dQ.

So, $\oint dQ/T=0$、$\oint dW/T=0$ or $\oint dE/T=0$ are untenable !

3. About boltzmann entropy

Then, what is boltzmann entropy?

Boltzmann entropy is a skill to demonstrate irreversibility —althought it doesn't give people more or less rigth and valuable content but play a part of misguidance.

In fact, liouville theorem applying to classical statistics and quantum statistics has demonstrated that boltzmann statistical entropy is not physical quantity — boltzmann statistical entropy can not calculate at all, however, liouville theorem is strict.

Second law of thermodynamics will be expounded by means of new method.

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