How and in What Sense Can the Entropy Be Measured?

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Abstract

In this paper, a method of measuring the entropy is presented. Problems related to the entropy and the heat are also discussed.

1 Introduction

Among the branches of classical physics, thermodynamics and statistical physics should be the most fantastic ones, which have attracted so many great minds to devote their lives and energy to investigating every topic in these fields. Perhaps among the branches of classical physics, they are the only ones that leave so many open questions, not only in the field of application, but also in their foundations.

In the last century, most of the physicists were attracted to the quantized physics, which can be viewed as the opposite side of classical physics. Although quantization has been the principal melody of physics ever since then, thermodynamics and statistical physics are still vivid with their own open questions. And, even in the so-called modern physics, shadows of thermodynamics and statistical physics are also seen: In the black hole theory, black holes are endowed with the temperature and the entropy[1]. Ideas and concepts of thermodynamics and statistical physics are also applied to the condensed matter theory and the string theory[2]. In fact, the history of quantum theory can be traced back to thermodynamics and statistical physics, where M. Planck use the famous assumption $E = h\nu$ to derive Planck’s formula[3], the spectral energy distribution of black bodies.

On the other hand, there are so many open questions in thermodynamics as well as statistical physics — there are even no universal theories, neither thermodynamic nor

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statistical, for non-equilibrium systems. Thus the foundations of thermodynamics, which are claimed to be valid for arbitrary thermal systems and arbitrary processes, could not be tested by comparing the experimental data with the predictions from a universal thermodynamics. This sounds not so nice to the society of physics.

It will benefit us greatly if we exam the foundations of thermodynamics carefully, no matter theoretically or experimentally. For example, if we were able to measure the entropy of a system in an arbitrary given state, it would be a piece of good news. However, whenever we try to fulfill such a scheme, we always find that there are some confusing points or experimental obstacles in thermodynamics, standing in the way to prevent us from approaching to our goal.

In this paper, a method is given as how to measure the entropy of a system in an arbitrary given state. In order to simplify our discussion, we assume it to be a gas system consisting of only one kind of molecules, with equilibrium states being labeled by its temperature $T$, its volume $V$ and the amount $n$ of its molecules measured in the unit of moles. As implied, such a system is an open system.

According to thermodynamics, a reversible process is adiabatic if and only if the entropy of the system is “conserved”, or, invariant, in the process. This statement is theoretically explicit, but it is hard to be applied in experiments. Usually a process is judged to be adiabatic empirically or a priori. In a thermodynamic measurement, one often wants to assure that a process is adiabatic, or that certain a system, which may consist of the system to be measured as well as some part of its surroundings, is thermally isolated from other surroundings. Hence, in thermodynamics, the error in a measurement concerning heat or thermodynamic functions are hard to be estimated quantitatively.

The situation becomes rather worse in the case of open systems because the concept of an adiabatic process is much far away from our heuristic ideas. Whenever the amount of molecules is changed in a reversible process, the entropy accompanying the molecules that is brought into or out of the open system accounts for certain part of the change of the entropy of the open system. As a matter of fact, an adiabatic reversible process, namely, a reversible process which remains the entropy invariant, will be peculiar from the point of view of empiricism: A reversible process that seems not to absorb or emit heat is not adiabatic provided the amount of molecules is changing. The detailed analysis is presented in §2.2, implying that there are serious problems in the theory of thermodynamics. But this will not be the topic of this paper.

The concept of heat thus is made confusing. It arises to be a question whether we can measure the heat correctly if one of the amounts of the components of a system is changed in a process. If there is no problem, then the method in this paper can be applied to measure the entropy of a system state by state.

This paper is organized as in the following. In §2, some points that might cause confusion or arguments are made clear first. Especially, the entropy of an open system, as well as the heat absorbed by it, is analyzed. It seems that the theory of thermodynamics of reversible processes is not compatible with the thermodynamic laws. It is indeed the case[4], but this is not the topic of this paper. In §3, we first outline of the method of how to measure the entropy of an equilibrium gas system. Then the formulas are derived in details. In §4, conclusions and further discussions are given.

For those who are interested in the measuring methods, §3.1 is what the wanted. Those who want to see the detailed derivation may find it in §3.2. If there is any question
about these contents, then §2 is referred to.

2 Problems That Should Be Made Clear

Before we start to discuss how the entropy could be measured, some problems should be made clear because the author astonishingly finds that there are so much misunderstanding when the topic of this paper is discussed. Those who does not want to quarrel with me, when he or she is reading the next section, may safely skip the following contents in this section. But when he or she feels eager to quarrel with me, I beg him or her to read this section carefully before he or she comes up to me.

In this paper, we only discuss the open systems consisting of one kind of molecules, with the amount denoted by \( n \) in the unit of moles. For simplicity, we assume that the system is a fluid system.

First let me emphasize that the correctness of thermodynamics of reversible processes should never be questioned in this paper, because I am trying to give some possible experimental methods, in its framework, of how to measure the entropy of a system in an equilibrium state. From the discussions, it can be revealed that there are some serious questions rooted deeply in thermodynamics. However, in order for the outline of this paper to be clear, the correctness of thermodynamics should never be suspected.

2.1 The Absolute Entropy and the Third Law of Thermodynamics

Perhaps someone wants to remind me that, in thermodynamics, functions such as the internal energy \( U \) and the entropy \( S \) can be determined only up to a constant, hence it should be suspected immediately that the absolute entropy, while not the change of it, could be measured.

However, one should recall that it is not the case, at all. When any one of the thermodynamic potentials such as the internal energy \( U \), the enthalpy \( H = U + pV \), the Helmholtz free energy \( F = U - TS \) or the Gibbs free energy \( G = U + pV - TS \), et al, is assumed to be additive and to be a homogeneous function of the first degree in its corresponding extensive variables, the arbitrariness of all the constants in these potentials and the entropy function ends up. For example, when \( G(T,p,n) \) is assumed to be a homogeneous function of the first degree in \( n \), it can be obtained that\[^3,4\]

\[
G = \mu n
\]

by using Euler’s theorem for homogeneous functions. Hence \( U, H \) and \( F \) are all obtained as in the following:

\[
\begin{align*}
U(V,S,n) &= -pV + TS + \mu n, \\
H(p,S,n) &= TS + \mu n, \\
F(T,V,n) &= -pV + \mu n.
\end{align*}
\]

Since \( dF = -pdV - SdT + \mu dn \), the entropy

\[
S = -\left(\frac{\partial F}{\partial T}\right)_{V,n} = S(T,V,n) \tag{2}
\]
is also determined\(^1\), being a homogeneous function of the first degree in \(V\) and \(n\). Such an entropy is what is suggested to be measured in this paper.

Someone may argue that this would make the third law of thermodynamics unnecessary. Is that true? Of course, no, because this is not the business that third law of thermodynamics can do. There are other conclusions, such as that the absolute zero of temperature cannot be reached by any finite process, that are not available without the third law.

Since there are various versions of the third law in literature, it is not strange that there are lots of gentlemen who think that the third law can be used to determine the integral constants in entropy\(^2\). Here we state the third law as that in [5]: For a system, the limit \(S_0 = \lim_{T \to 0} S\) is a constant value that is independent of any variables such as the volume \(V\), the pressure \(p\) and the amount \(n\), et al. It is in this sense that the determination of \(S_0\) is not the business of the third law only.

The third law of the thermodynamics concerns only the asymptotic behavior of the entropy. It is a relatively independent thing to determine the constant \(S_0\) for a system. Unfortunately, in the literature it is often boldly assumed that \(\lim_{T \to 0} S = 0\) as soon as the third law has been described. Even Sommerfeld could not prevent from doing so\(^3\). One may ask the author who did so: Does \(\lim_{T \to 0} S = 0\) contradict with the assumption such as that the Helmholtz free energy \(F\) is a homogeneous function of the first degree in extensive variables \(V\) and \(n\), et al? If no, is such an assumption independent of the third law?

In fact, \(\lim_{T \to 0} S = 0\) is a corollary of such an assumption together with the third law: According to eq. (2), \(S_0(V, n) = \lim_{T \to 0} S(T, V, n)\) is a homogeneous function of \(V\) and \(n\), say. At the same time, it is a constant as asserted by the third law of thermodynamics. Hence, using Euler’s theorem, we obtain

\[
S_0 = \frac{\partial S_0}{\partial V} V + \frac{\partial S_0}{\partial n} n = 0.
\]

To my opinion, the assumption that a particular thermodynamic potential is a homogeneous function in its corresponding extensive variables is and must be independent of the third law. One may name such an assumption as the fourth law of thermodynamics, if he likes to. As a consequence, the belief that each of thermodynamic potentials as well as the entropy can be determined only up to a constant\(^4\) is incorrect.

\(^1\)To be more confirmative, suppose that \(S' = S + S_0\) is another possible entropy for the same system in the same state, with \(S_0\) a constant. Then we obtain another Gibbs free energy \(G' = G - TS_0 = \mu n - TS_0\), which is no longer a homogeneous function in \(n\) whenever \(S_0 \neq 0\). Constants in other functions can be similarly discussed.

\(^2\)For example, it is written in the famous book\(^5\) of L. D. Landau and E. M. Lifshitz, saying that the entropy of any system vanishes at the absolute zero of temperature. According to A. Sommerfeld, however, W. Nernst disliked the concept of entropy\(^6\). If so, it seems that the description of Nernst’s theorem in [5] is not a faithful version of Nernst’s original statement. And, whatsoever speaking, Sommerfeld’s description is the representative of the version that is widely accepted, although, in spirit, it is equivalent to Landau and Lifshitz’s statement in [5]. As for the reason why they are equivalent, see the next two paragraphs.

\(^3\)Strictly speaking, the potentials \(F\) and \(G\) both have two constants before they are fixed. For example, let \(S\) and \(S' = S + S_0\) describe the same system in the same state, and let the internal energies \(U\) and \(U' = U + U_0\) describe also the same system in the same state. Then the corresponding Helmholtz free
2.2 The Entropy and the Heat

How to calculate the heat that is absorbed by an open system? If the process is reversible, then, according to thermodynamics, the heat absorbed by the open system is \( dQ = T \, dS \) where \( dS \) is the total differential of the entropy of that open system. The answer is so simple that it seems absurd to ask such a question. However, the following analysis indicates that the so-called adiabatic process, which is a reversible process with the entropy \( S \) remaining to be constant, is not a process as we have expected from the word adiabatic.

First let us consider a simple example.

Suppose that there is a fluid system consists of one kind of molecules amounted as \( n_0 \). The system is in equilibrium at a temperature \( T \) and a volume \( V_0 \). Then, according to the zeroth law of thermodynamics, there should be no heat transferred from one part of it to another. Meanwhile, the internal energy of this system is \( U_0 = -pV_0 + TS_0 + \mu n_0 \) where \( S_0 \) is the entropy of the system, as indicated by eq. (1).

Now let us consider a subsystem of it which has a virtual boundary that separates the subsystem from the whole. Suppose that the virtual boundary of the subsystem expands slowly such that the center of mass remains unchanged and the process can be considered as reversible. The subsystem is obviously an open system, whose state is denoted by \( (T, V, n) \) with an entropy \( S = S(T, V, n) \).

Since the virtual boundary and the process are just imaginary, the intensive quantities \( p \), \( T \) and \( \mu \) are constant. Assume the initial and the final states of the subsystem are \( (T, V_1, n_1) \) and \( (T, V_1 + \Delta V, n_1 + \Delta n) \), respectively, then

\[
\frac{\Delta V}{V_0} = \frac{\Delta S}{S_0} = \frac{\Delta n}{n_0}.
\]

Hence, according to the formulism of thermodynamics, certain amount of heat \( Q = T \, \Delta S \neq 0 \) must be absorbed by the subsystem after its virtual expansion. In other words, as a virtual closed surface moves in an equilibrium system, one has to admit that certain an amount of heat as \( dQ = T \, dS \) has been transferred through it, accompanying the substance that goes through the surface, even though the system is in equilibrium.

Then questions arise immediately. First, we have seen that the above subsystem, separated by a virtual surface, does absorb some heat if its volume has been changed. On the other hand, however, the zeroth law of thermodynamics should have repelled such a possibility, because heat will not be transferred between two systems or two parts of a system provided there is no difference of temperature. Secondly, ever since the first law of thermodynamics was accepted, heat has been treated as a form of energy transfer, being no longer anything accompanying the ordinary substance as that was insisted in the caloric theory. Now it seems that the caloric theory is somehow restored in thermodynamics.

So, there are serious questions in thermodynamics. We leave these questions to be discussed in [4]. However, we must make our viewpoints to these questions clear before we perform further discussions.

(1) For a system, the heat absorbed by it in a reversible process is always calculated to be \( dQ = T \, dS \), no matter whether it is an open system or not. To say a reversible process

energies will be \( F = U - TS \) and \( F' = U' - TS' = F + U_0 - TS_0 \), respectively. The same thing happens in the Gibbs free energy: \( G' = G + U_0 - TS_0 \). Rigorously, all the potentials can be determined up to at most two constants before they are fixed: One comes from the internal energy, and the other comes from the entropy.
is adiabatic, it is equivalent to say that \( dS = 0 \) in the process. As a consequence, in order that a reversible process is adiabatic if certain a number of molecules have been brought into the system, it must emit a suitable quantity of heat into the surroundings, because the newly added molecules always tend to increase the total entropy of the open system. Therefore the concept of adiabatic processes is far away from what we have expected intuitively. \textit{As for how a process can be identified to be adiabatic in the experiments, it is not the topic of this paper.}\)

(2) For simplicity, we only discuss open systems consist of only one kind of molecules. When the amount \( n \) of the molecules in the open system are changed, the contribution of the newly added molecules to the entropy has been included in \( dS \), because \( S \) depends on \( n \), too, as shown in eq. (3). If the amount of molecules in the system remains constant, the change of entropy in a reversible process is given by

\[
\left( \frac{\partial S}{\partial T} \right)_{V,n} dT + \left( \frac{\partial S}{\partial V} \right)_{T,n} dV.
\]

For a reversible process in which the amount \( n \) is changing, the contribution of the added molecules is

\[
\left( \frac{\partial S}{\partial n} \right)_{T,V} dn,
\]

and the total differential of the entropy, \( dS \), is the sum of the above two parts. In terms of \( dS \), the contribution of the added molecules needs not to be considered any more.

As an example, let us consider the fluid system with an open subsystem enclosed by a virtual boundary, as introduced formerly. When the virtual boundary is changed, the total change of the entropy of the subsystem consists of two parts:

\[
\left( \frac{\partial S}{\partial V} \right)_{T,n} dV + \left( \frac{\partial S}{\partial n} \right)_{T,V} dn.
\]

Due to the fact that \( dV = \frac{dn}{n} \) where \( V \) and \( n \) are the volume and the amount of molecules of the subsystem, respectively, one needs not to know the details of the entropy function, yielding

\[
\left( \frac{\partial S}{\partial V} \right)_{T,n} dV + \left( \frac{\partial S}{\partial n} \right)_{T,V} dn = \left( \frac{\partial S}{\partial V} \right)_{T,n} \frac{V}{n} dn + \left( \frac{\partial S}{\partial n} \right)_{T,V} \frac{dn}{n} = \left[ V \left( \frac{\partial S}{\partial V} \right)_{T,n} + n \left( \frac{\partial S}{\partial n} \right)_{T,V} \right] \frac{dn}{n} = S \frac{n}{n} dn = S \frac{V}{V} dV.
\]

Since both \( S = \frac{S}{n_0} \) and \( V = \frac{V}{V_0} \) remain constant in the process, we can integrate the above to give

\[
\Delta S = \frac{S_0}{n_0} \Delta n = \frac{S_0}{V_0} \Delta V,
\]

coinciding with eqs. (3). Obviously, if one is about to consider the contribution of the molecules that flows into the subsystem once again, he is definitely doing something wrong.
Is heat a kind of substance accompanying ordinary matter, as it was said in the old-fashioned caloric theory, or just the energy transferred from one body to another as the result of the difference of temperature? As we know, thermodynamics has chosen the latter. But the following consideration will make thermodynamics to sink into trouble.

As what happens in $dS$, whenever a process is reversible, the heat

$$dQ = TdS = T \left( \frac{\partial S}{\partial T} \right)_{V,n} dT + T \left( \frac{\partial S}{\partial V} \right)_{T,n} dV + T \left( \frac{\partial S}{\partial n} \right)_{T,V} dn$$

consists of two parts: the ordinary part $C_{V,n} dT + T \left( \frac{\partial S}{\partial V} \right)_{T,n} dV$ and the heat “brought into the system by $dn$”, $T \left( \frac{\partial S}{\partial n} \right)_{T,V} dn$. The latter makes the heat something like the companion of the ordinary substances. Thus, reasonably, some of us will feel uncomfortable because the spirit of the caloric theory is found wandering in thermodynamics. But we do not want to discuss it, but leaving it into \[4\].

### 3 How to Measure the Entropy

#### 3.1 The Outline of the Measuring Methods

For simplicity we only consider the gas systems, each of which consists of only one kind of molecules. For such a system, its equilibrium state can be specified by three variables, the absolute temperature $T$, the volume $V$, and the amount $n$ of the molecules, say. Then there are the equations of state for such a system. One of these equations is $p = p(T, V, n)$, which can be obtained state by state. The partial derivatives of $p$ with respect to $T$, $V$ and $n$, respectively, can also be measured state by state.

In order to measure the entropy $S = S(T, V, n)$ of such a system in a given state $(T, V, n)$, suppose that there is a reversible isothermal process

$$T = \text{constant}, \quad V = V(n).$$

Let $(T, V, n)$ and $(T, V + dV, n + dn)$ be the states in the above process, with $dQ$ the heat that is absorbed by the system. Then the entropy of the system in the state $(T, V, n)$ is

$$S(T, V, n) = \frac{n}{T} \frac{dQ}{dn} + \left( \frac{\partial p}{\partial T} \right)_{V,n} \left( V - n \frac{dV}{dn} \right).$$

Therefore the entropy can be obtained provided that $dQ$ has been obtained. Especially, if the process is both isothermal and adiabatic, namely, $T = \text{constant}$ and $dQ = 0$, the entropy in the state $(T, V, n)$ will be

$$S(T, V, n) = \left( \frac{\partial p}{\partial T} \right)_{V,n} \left( V - n \frac{dV}{dn} \right).$$
3.2 The Principles of the Experiment

As we know, for a gas system, the first law of thermodynamics can be written in the form of

\[ dU = -p \, dV + T \, dS + \mu \, dn. \]

A Legendre transformation gives the differential of the free energy as

\[ dF = -p \, dV - S \, dT + \mu \, dn, \tag{8} \]

where the free energy is defined as \( F = U - TS \). Being a homogeneous function of the first degree in \( V \) and \( n \) for any given temperature \( T \), Euler’s theorem for homogeneous functions of the first degree must be satisfied, in which the temperature is treated as a parameter, giving

\[ F = -pV + \mu n. \tag{9} \]

The optional form of the above equation can be \( U = -pV + TS + \mu n \) for the internal energy, or \( G = \mu n \) for the Gibbs free energy, as what have been mentioned in §2.1.

One of the most important consequences of the above equations is that the intensive quantities \( p, T \) and \( \mu \) are not functionally independent, namely, their differentials are constrained by an equation

\[ d\mu = \frac{V}{n} \, dp - \frac{S}{n} \, dT. \tag{10} \]

In fact, it can be obtained by the comparison of the differential of eq. (9) with eq. (8). The above equation implies that the chemical potential \( \mu \) is a function of the intensive variables \( p \) and \( T \). Since the pressure \( p \) can be viewed as a function of the variables \( T, V \) and \( n \), we can obtain

\[ \left( \frac{\partial \mu}{\partial T} \right)_{V,n} = \frac{V}{n} \left( \frac{\partial p}{\partial T} \right)_{V,n} - \frac{S}{n}, \tag{11} \]

by using the chain rule of partial derivatives.

By virtue of the above equation, the heat that is absorbed by an open system in a reversible process reads

\[ dQ = T \, dS = C_{V,n} \, dT + T \left( \frac{\partial p}{\partial T} \right)_{V,n} \, dV + \frac{T}{n} \left[ S - V \left( \frac{\partial p}{\partial T} \right)_{V,n} \right] \, dn, \tag{12} \]

in which the partial derivatives of the entropy \( S \) with respect to \( V \) and \( n \), respectively, have been replaced by the partial derivatives of \( p \) and \( -\mu \), both with respective to \( T \), according to Maxwell’s relations

\[ \left( \frac{\partial S}{\partial V} \right)_{T,n} = \left( \frac{\partial p}{\partial T} \right)_{V,n}, \quad \left( \frac{\partial S}{\partial n} \right)_{T,V} = -\left( \frac{\partial \mu}{\partial T} \right)_{V,n}. \tag{13} \]

As we know, the heat capacity \( C_{V,n} \) in eq. (12) is defined as

\[ C_{V,n} = T \left( \frac{\partial S}{\partial T} \right)_{V,n}. \]

For an isothermal reversible process (5), we obtain the equation

\[ \frac{dQ}{dn} = T \left( \frac{\partial p}{\partial T} \right)_{V,n} \, dV + \frac{T}{n} \left[ S - V \left( \frac{\partial p}{\partial T} \right)_{V,n} \right] \, dn \]

from eq. (12). Hence eq. (5) can be obtained. If the process (5) is not only isothermal, but also adiabatic, then \( dQ = 0 \). Thus eq. (7) can be obtained.
4 Conclusions and Discussions

In §2.1, it was concluded that the concept of abstract entropy makes sense in thermodynamics. So there should be some methods to measure the entropy. The method presented in this paper is one of them.

As we have indicated in §3, were it possible that (1) we can design an infinitesimal reversible process that is isothermal with the amount $n$ of molecules being changed and that (2) we can measure the heat absorbed by the open system in this process, then the entropy of the system can be measured. If, (3) in addition, the infinitesimal process is adiabatic, it could not be better.

However, we have seen in §2.2 that the concept of heat in thermodynamics is not so simple as it looks. It seems to be a question whether we can measure the heat if, in the process, any one of the amounts of the components is changed. This is due to the fact, in thermodynamics, that the molecules that are brought into or out of an open system are accompanied with certain a quantity of heat, as shown in the example of the subsystem of an equilibrium fluid system (see, §2.2). As a consequence, it can be asked whether the method presented in this paper is practical.

We must notice that, in order to measure the entropy $S(T, V, n)$ in a given state $(T, V, n)$, one process satisfying the conditions (1) and (2) in the above is sufficient. If there is no such a reversible process, we may refer to thermodynamics as a theory speaking of nothing. As long as we believe in thermodynamics, we have to admit that the method of measuring the entropy is reasonable and practical.

It is in this sense that the entropy can be measured.

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