The Physical Meaning of Entropy–1*

Effect of Change in Volume on Entropy

Nirupam Rohatgi

The article explains the physical significance of ‘entropy’ based on the definition of entropy in statistical thermodynamics. The effect of temperature on entropy will be discussed in the next article.

Introduction

In classical thermodynamics, entropy is defined as $\Delta S = \int_{rev} \frac{\delta Q}{T}$, i.e., the change in entropy of a closed system is the amount of heat given to the system divided by the absolute temperature of the system at which heat was added to the system, as the system moves along a reversible path. However, the physical meaning of this expression is not obvious, and it is loosely defined as a measure of the degree of randomness. This explanation is specious, for randomness is a subjective concept, and there is no scientific way to measure the degree of randomness.

Entropy has another formulation in statistical thermodynamics, which beautifully explains the physical significance of entropy. The objective of this article is to highlight the equivalence between the two formulations of entropy, and explain the physical meaning of entropy.

Entropy in Classical Thermodynamics

Before we move on to entropy, let us revisit the first law of thermodynamics in brief. The first law of thermodynamics is also known as the law of conservation of energy. It says that “Energy

*Vol.25, No.12, DOI: https://doi.org/10.1007/s12045-020-1093-9
The second law of thermodynamics identifies another set of processes, which follow the law of conservation of energy, but they are still not feasible.

The second law of thermodynamics states that any process in which the entropy of the Universe decreases is not feasible.

can neither be created nor destroyed”. In other words, it means that a process in which energy is not conserved is impossible. This assertion (or the law) leads to the discovery of a property called the ‘internal energy’.

The second law goes a step further and explores another set of processes that follow the first law or the law of conservation of energy, but they are still not feasible. For example:

- The spontaneous flow of heat from a reservoir at low temperature to a reservoir at high temperature.
- Automatic separation of a mixture of two gases into its constituents.
- Running a power plant by extracting energy from the atmosphere (or running an engine that will receive heat from a single reservoir and do an equivalent amount of work on the surroundings without rejecting any heat to any reservoir).

It has been observed that the above processes and many other processes that obey the first law are not feasible. The second law of thermodynamics explores such processes. It says that whenever a closed system undergoes a reversible or irreversible cyclic process,

\[ \oint \frac{\delta Q}{T} \leq 0, \quad (1) \]

and if the closed system undergoes a reversible cyclic process,

\[ \oint_{\text{rev}} \frac{\delta Q}{T} = 0, \quad (2) \]

where,

\[ \delta Q = \text{Heat given to the system by the surroundings, and} \]
\[ T = \text{temperature of the system at which heat is being given to the system.} \]

Equation (2) indicates the existence of a property that is independent of the path and depends only on the state of the system. This property is named entropy \((S)\), and it is defined as:
\[ \Delta S = \int_{\text{rev.1}}^{2} \frac{\delta Q}{T} \] (3)

It may be noted here that while heat given to a closed system \((Q)\) is a path function, \(\int \frac{\delta Q}{T}\) over a reversible path turns out to be a state function. Mathematically, when the cyclic integral of a function involving one or more path functions is equal to zero, we can define a new property. We know that in the case of the first law, when \(\oint (\delta Q - \delta W) = 0\), which involves two path-functions, we define internal energy as a property. Similarly, when \(\oint_{\text{rev}} \frac{\delta Q}{T} = 0\), which involves \(Q\)—a path function—we define entropy as a property. (If, however, \(Q\) were a state function and since \(T\) is already a state function, there would have been no possibility of defining a new property of a system.)

The physical meaning of entropy is still to be explained. We understand ‘heat’ and ‘temperature’ well and can correlate them to our day to day experiences. However, we don’t know the physical meaning of ‘heat’ divided by ‘temperature’, i.e., \(\frac{Q}{T}\). Thus, we are not able to understand the physical significance of ‘entropy’.

In classical thermodynamics, entropy is loosely defined as a measure of the degree of randomness. This explanation is specious, for randomness is a subjective concept. There is no scientific way to measure the degree of randomness. Classical thermodynamics doesn’t go beyond this.

Thus, the question remains—“what is entropy?”

The answer to this puzzle lies in ‘statistical thermodynamics’.

**Macro vs Microstructure**

Before we proceed to understand entropy as explained in statistical thermodynamics, let us refresh certain concepts we have studied earlier that we are going to encounter in the following text.

We know that matter is made of tiny invisible atoms. Any system which consists of material is nothing but an ensemble of a large number of atoms. For example, 29 g of air contains about...
6.022 × 10²³ molecules of oxygen, nitrogen, and other minor constituents—really a very huge number!

Since a system contains matter and matter is made of a large number of molecules, any system would possess two sets of structures. One, that is gross, visible to our eyes and perceptible to our senses, is called the macrostructure. The other, that is hidden, pertains to the distribution of atoms and can be understood only statistically is called the microstructure.

Let us elaborate on it further. Consider a given quantity of an ideal gas at a fixed temperature and pressure. We know from the state postulate¹ that once any two thermodynamic properties of a pure substance are fixed, all the remaining six thermodynamic properties of the gas are also fixed. The thermodynamic properties represent the macrostate or the macrostructure of the gas. Thus, from the thermodynamics point of view, or macroscopically, the gas is in a steady-state, i.e., all its properties are fixed. But is the gas really in a steady-state? No! Not at all!

The molecules of the gas are moving randomly, crisscrossing the whole volume, colliding with the wall and with other molecules on the way at a great speed and frequency. The gas is not at all in a static state. The gas is changing from one microstate to another microstate very rapidly, while at the macro level, all is uniform and steady.

Each different distribution of molecules represents a different microstate. Thus, for a given macrostate, a very large number of microstates exist.

Classical thermodynamics is concerned only with the macrostructure of the system and deals with any system in terms of its thermodynamic properties. It overlooks the great activity going on at the micro-level. On the other hand, as we shall learn in the following text, entropy is all about microstates. It is, for this reason, that classical thermodynamics fails to explain entropy.
Entropy in Statistical Thermodynamics

Unlike classical thermodynamics, statistical thermodynamics talks of microstates.

In statistical thermodynamics, entropy \( S \) is defined as

\[
S = k \ln(m),
\]

(4)

where,

- \( m \) = number of microstates a system possesses for a given macrostate,
- \( k \) = Boltzmann’s constant.

In other words, entropy is nothing but a function of the microstates of a system.

Is this definition of entropy in line with what we know about entropy from classical thermodynamics? Let us see.

Isothermal Expansion of a Gas: Change in Entropy Using Statistical Thermodynamics

In the following text, we are going to find out the change in the entropy of a gas due to a change in its volume at a constant temperature using the statistical definition of entropy.

Let us divide the volume containing the gas into cells such that the volume of each cell is equal to the volume of one molecule.

Let the number of cells in the volume = \( Z \), and the number of molecules present in the gas = \( N \).

We know that \( N \) molecules of gas can move around within volume \( V \) containing \( Z \) cells, in any way they like, subject to the condition that each molecule of the gas can occupy only one of the empty cells.

We also know from statistics that the number of ways \( N \) molecules can fill volume \( V \) is given by:
where, \( m \) = number of possible microstates and \( Z C_N \) represents the number of ways \( N \) particles can fill \( Z \) vacancies when identical particles are not identified separately.

This is a very large number and cannot be calculated directly. To calculate this number, we use an approximation (6) given below. The solution for the same is given separately in the Appendix.

\[
\ln(m) = N \ln \left( \frac{Z}{N} \right) + N. \tag{6}
\]

Now, let the volume of gas be increased from \( V_1 \) to \( V_2 \), such that \( \frac{V_2}{V_1} = r \).

The number of cells, then, would also increase by the same proportion, i.e., from \( Z_1 \) to \( Z_2 \), such that \( \frac{Z_2}{Z_1} = r \). Thus,

\[
\frac{V_2}{V_1} = \frac{Z_2}{Z_1} = r. \tag{7}
\]

However the number of molecules (\( N \)) remains the same. Let us now calculate the number of microstates for the two states having the same temperature (\( T \)) and volumes, \( V_2 \) and \( V_1 \).

\[
\ln(m_2) = N \ln \left( \frac{Z_2}{N} \right) + N, \tag{8}
\]

\[
\ln(m_1) = N \ln \left( \frac{Z_1}{N} \right) + N, \tag{9}
\]

\[
\Rightarrow \ln \left( \frac{m_2}{m_1} \right) = N \ln \left( \frac{Z_2}{Z_1} \right) - N, \tag{10}
\]

\[
\Rightarrow \ln \left( \frac{m_2}{m_1} \right) = N \ln \left( \frac{Z_2}{Z_1} \right). \tag{11}
\]

Let us now go back to the definition of entropy, i.e., equation (4).
\[ S = k \ln(m). \]

\[ \implies \Delta S = k \ln\left( \frac{m_2}{m_1} \right). \] (12)

Substituting the value of \( \ln\left( \frac{m_2}{m_1} \right) \) from equation (11), we get

\[ \implies \Delta S = kN \ln\left( \frac{Z_2}{Z_1} \right). \] (13)

Again substituting the value of \( \left( \frac{Z_2}{Z_1} \right) \) from equation (7), and multiplying and dividing by \( N_0 \), we get:

\[ \implies \Delta S = \left( \frac{N}{N_0} \right) kN_0 \ln\left( \frac{V_2}{V_1} \right). \] (14)

We know that

\[ n = \left( \frac{N}{N_0} \right) \text{ and } kN_0 = R, \] (15)

where, \( R = \) universal gas constant, \( N_0 = \) Avogadro’s number, and \( n = \) number of moles of the gas.

Thus,

\[ \implies \Delta S = nR \ln\left( \frac{V_2}{V_1} \right). \] (16)

We know from classical thermodynamics that the change in entropy of an ideal gas is given as:

\[ \implies \Delta S = nC_v \ln\left( \frac{T_2}{T_1} \right) + nR \ln\left( \frac{V_2}{V_1} \right). \] (17)

If the gas undergoes isothermal expansion, the change in entropy of the ideal gas is:

\[ \implies \Delta S = nR \ln\left( \frac{V_2}{V_1} \right). \] (18)
Thus, we find that the change in Entropy of an ideal gas undergoing isothermal expansion, obtained from the statistical thermodynamics and the classical thermodynamics are same.

Summary

Classical thermodynamics is concerned only with the macrostates of a system. Therefore, it explains entropy in terms of heat and temperature that represents the system and the process it undergoes from a macroscopic point of view. It gives the mathematical formulae for the change in entropy \( \int_{rev}^{2} \frac{\delta Q}{T} \), but it is unable to explain the physical meaning of entropy.

Statistical thermodynamics deals with the microstates of a system and defines entropy as a function of the number of microstates a system can possess for a given macrostate. It says that entropy is proportional to the log (base natural) of the number of microstates a system can possess, i.e., \( S = k \ln(m) \).

In the present article, it has been shown that for an ideal gas, the change in entropy due to the change in volume is the same for classical thermodynamics and statistical thermodynamics.

Box 1. Appendix

The solution of the equation (6), i.e.,

\[
\ln(m) = N \ln \left( \frac{Z}{N} \right) + N
\]

for \( N \ll Z \) is given below. The solution of the above equation is based on following the approximation.

\[
\ln(N!) = N \ln(N) - N.
\]  \hspace{1cm} (19)

The number \( N \) used above is very large. It is of the order of Avogadro’s number, and it is not possible to find \( \ln(N!) \) directly.

Contd.,
Box 2. Continued.

Therefore, we use the above equation to find the approximate value of \( \ln(N!) \). The following table gives error in equation (20), for very small values of \( N \). We find that as the value of \( N \) increases, the difference between the two sides of the equation decreases continuously. Even for \( N = 170 \), the difference between both the sides of the equations is only 0.5\%, which will be almost negligible as we approach the actual value of \( N \).

**Error in calculation of \( \ln(N!) \) when using its approximation \([N \ln(N) - N]\).**

<table>
<thead>
<tr>
<th>( N )</th>
<th>( (N!) )</th>
<th>( \ln(N!) )</th>
<th>( N \ln(N) - N )</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.04E + 64</td>
<td>148.4778</td>
<td>145.6012</td>
<td>1.94</td>
</tr>
<tr>
<td>100</td>
<td>9.33E + 157</td>
<td>363.7394</td>
<td>360.517</td>
<td>0.89</td>
</tr>
<tr>
<td>150</td>
<td>5.71E + 262</td>
<td>605.0201</td>
<td>601.5953</td>
<td>0.57</td>
</tr>
<tr>
<td>170</td>
<td>7.26E + 306</td>
<td>706.5731</td>
<td>703.0857</td>
<td>0.49</td>
</tr>
</tbody>
</table>

\[ m = e^{C_N} = \frac{Z!}{N!(Z-N)!}. \] (20)

\[ \ln(m) = [Z \ln(Z) - Z] - [N \ln(N) + N] - [(Z - N) \ln(Z - N) + (Z - N)], \] (21)

\[ \Rightarrow \ln(m) = Z \ln(Z) - N \ln(N) - (Z - N) \ln(Z - N), \] (22)

\[ \Rightarrow \ln(m) = (Z - N) \ln(Z) + N \ln(Z) - N \ln(N) - (Z - N) \ln(Z - N), \] (23)

\[ \Rightarrow \ln(m) = (Z - N) \ln\left(\frac{Z}{Z - N}\right) + N \ln\left(\frac{Z}{N}\right), \] (24)

\[ \Rightarrow \ln(m) = N \ln\left(\frac{Z}{N}\right) - (Z - N) \ln\left(\frac{Z - N}{Z}\right), \] (25)

\[ \Rightarrow \ln(m) = N \ln\left(\frac{Z}{N}\right) - (Z - N) \ln\left(1 - \frac{N}{Z}\right), \] (26)

\[ \Rightarrow \ln(m) = N \ln\left(\frac{Z}{N}\right) - Z \left(1 - \frac{N}{Z}\right) \ln\left(1 - \frac{N}{Z}\right), \] (27)

\[ \text{if } N << Z, \text{ i.e., } \frac{N}{Z} << 1 \]

\[ \Rightarrow \ln(m) = N \ln\left(\frac{Z}{N}\right) - Z \left(\frac{-N}{Z}\right), \] (28)

\[ \Rightarrow \ln(m) = N \ln\left(\frac{Z}{N}\right), \] (29)

\[ \Rightarrow \ln(m) = N \ln\left(\frac{Z}{N}\right) + N. \] (30)
Suggested Reading