Extensivity of entropy

S K Das
Department of Physics, Maulana Azad College, 8 Rafi Ahmed Kidwai Road, Calcutta 700 013

and

S Sengupta
B 15/4, Kalyani, Nadia, West Bengal 741 235

Received 27 February 2003; accepted 6 October 2003

In the conventional framework of thermodynamics it is an established fact that, in absence of surface effects, infinitesimal change in entropy is extensive. But this does not automatically guarantee the extensivity of entropy. Our purpose in this paper is to discuss this problem, strictly within the framework of thermodynamics, using a principle of linear superposition in conjunction with a simple postulate, which contains a feature consistent with quantum mechanical concept of indistinguishability of atoms and molecules. Some important consequences of the extensivity of entropy are also discussed. Extensivity of entropy is essential to calculate the change in entropy in an adiabatic irreversible process where the number of atoms of a system is not fixed as well as to make thermodynamics free from the well-known Gibbs paradox.

Keywords: Entropy, Thermodynamics, Extensivity of entropy, Gibbs paradox

1 Introduction

In a recent paper on the problem of extensivity of entropy, Addison & Gray have concluded that, entropy (S), as defined in thermodynamics, need not necessarily be an extensive quantity. The change of entropy is defined by Clausius as:

$$\Delta S = \frac{1}{T} \int \frac{\delta Q}{T}$$  \hspace{1cm} ...(1)

where the mass (M) or the number (N) of particles in the system remains fixed and nothing can be concluded about how the change of entropy is related to mass or the number of particles. Addison & Gray further assert that the formula:

$$\delta Q = T \, dS = dU + A \, dB$$  \hspace{1cm} ...(2)

(\delta W = A \, dB, A is an intensive parameter and B is extensive) does not prove that, even dS is an extensive quantity, because dU is not in general extensive. In the presence of very long-range mutual interactions between the constituent particles, U may cease to be proportional to N or M. The authors' further demonstrate that, "systems in which entropy is an extensive quantity are systems in which entropy obeys a generalized principle of linear superposition".

Without going into the question whether a system, in which very long range mutual interaction (such as, the Coulomb force between charged particles, and the gravitational attraction between two point masses) exists and internal energy U is non-extensive, can be properly handled within the framework of classical thermodynamics, it is discussed in the present paper, an alternative problem concerning the extensivity of entropy.

In the basic thermodynamic equation for a two variable system as given in Eq. (1), the authors confine to systems which are (i) homogeneous, (ii) surface effects are negligible and (iii) very long-range mutual interactions among the constituents are absent.

They also assume that, there is no non-uniform external potential field. Then it follows that dU is an extensive quantity. This is also supported by empirical evidence. Also B and dB are extensive quantities. It follows that, dS is also an extensive quantity. The problem is, does it follow that, in this case, S itself must be an extensive quantity? The implication is that, the constant of integration must be proportional to N or M. It is well-known that, in classical statistical mechanics for a perfect gas, the
constant comes out to be proportional to $N \ln N$, creating the well-known Gibbs paradox.

Comments from standard textbooks in connection with the present problem will be interesting. Landsberg\(^1\) asserts the extensivity of entropy in the form of a law, which he calls the fourth law of thermodynamics. The phase space of conventional thermodynamics is restricted by the requirement that, $N$ remains constant. Landsberg denotes this phase space by $E$. With the introduction of the fourth law, the constraint on $N$ is removed and the thermodynamic phase space gets enlarged to what Landsberg\(^2\) calls $F$. For thermodynamics to be meaningful, it becomes necessary that, any two points in this larger phase space can be connected by reversible paths. Landsberg asserts this point, but does not indicate how such a path can be realized in practice.

According to Reif\(^3\) $S$ is an extensive quantity. This is supposed to follow from the relation $\Delta S = \int \frac{\delta Q}{T}$, since the heat absorbed $\delta Q = C \, dT$ (C, the heat capacity) is an extensive quantity. Similar statement has been made by Kauzmann\(^4\), Fermi\(^5\) mentions that, extensivity of $S$ is ensured only if surface effects are ignored. Riedi\(^6\) concludes that extensivity of $S$ is necessary to show that $\Delta S = 0$, in self-diffusion. With reference to the statement of Reif\(^3\) and Kauzmann\(^4\) it may be noted that there is some confusion. The authors have already pointed out that, the extensivity of $\Delta S$ does not automatically guarantee the extensivity of $S$. The purpose of this paper is to clarify the confusion that exists, and seek a solution to this problem strictly within the framework of classical thermodynamics, which is independent of any model.

2 Problem of Self-diffusion in Thermodynamics

In classical thermodynamics, there is a closely related problem. It is the problem of self-diffusion i.e., diffusion between systems having identical chemical constitution. Let us imagine two thermodynamic systems with identical gases, separated by an adiabathic partition having a window at the middle. The temperature and pressure in both chambers are the same. If now the window is opened, will there be an increase in entropy because of diffusion of molecules in the left chamber into the right chamber and vice versa? If the gases in the two chambers are chemically different, it can be demonstrated that, entropy will increase and for this we do not have to assume any particular equation of state\(^7\). The essential element in this demonstration is the existence of semi-permeable membranes, which allow only one type of molecules to pass through it, while obstructing the other. When both chambers have the same type of molecules, we need semi-permeable membranes which will preferentially allow only the right (left) hand molecules to pass through and obstructing the left (right) hand molecules. The authors postulate that, such membranes do not exist and hence no self-diffusion occurs between two such systems. Hence, it can be asserted that, no change in entropy occurs when, in the thought experiment, the window of the partition is opened. This is confirmed by the fact that, no change in properties like, temperature and pressure occur. This is further corroborated by the statement of Landsberg\(^2\) who brings out the point that, insertion (or withdrawal) of adiabatic walls does not affect the properties of systems of identical molecules, in connection with what he calls the basic trick of thermodynamics. The above postulate is consistent with the quantum statistical assertion that, in calculating the statistical probability of dynamical states, atoms or molecules of a particular chemical species must be regarded as indistinguishable, that is, no membrane can distinguish between the molecules in the left chamber from those in the right chamber. This statement is the thermodynamic equivalent of the quantum mechanical statement of indistinguishability of atoms and molecules.

3 Proof that Entropy Must be Extensive

Consider two distinct thermodynamic systems separated by an adiabathic partition wall having a window $W$ at the middle (Fig. 1). Both systems contain the same molecules in different numbers $N_1$ and $N_2$. The thermodynamic equations for the two systems are:

\[ T_1 \, d \, S_1 = d \, U_1 + p_1 \, d \, V_1 \quad \ldots (3) \]

and

\[ T_2 \, d \, S_2 = d \, U_2 + p_2 \, d \, V_2 \quad \ldots (4) \]

where $S_1$, $U_1$ depend on $N_1$ and $S_2$, $U_2$ depend on $N_2$. If the two systems are now put in thermal contact, say, by making the base thermally conducting, and putting the same weights on the two pistons in the two cylinders having the same cross-sections,
pressures in the two gases will be the same. The two simple thermodynamic systems are now changed into a single complex system defined by the equation:
\[ T \, d \left( S_1 + S_2 \right) = d \left( U_1 + U_2 \right) + p \, d \left( V_1 + V_2 \right) \] ... (5)
or
\[ T \, d S = d U + p \, d V \] ... (6)
where, \( U = U_1 + U_2 = U \left( N_1 + N_2 \right) \) and \( V = V_1 + V_2 = V \left( N_1 + N_2 \right) \), as both these quantities are extensive. But, \( S = S \left( N_1, N_2 \right) = S \left( N_1 \right) + S \left( N_2 \right) \) and we cannot write this in the form \( S \left( N_1 + N_2 \right) \). Eq. (5) can be interpreted as a linear superposition law, where two different thermodynamic systems are superposed to generate a single thermodynamic system. If now we open the window (W) between the two cylinders, then there will be no change in any thermodynamic property because no self-diffusion takes place. In the final state there is now a simple homogeneous system of \( \left( N_1 + N_2 \right) \) particles whose entropy is \( S \left( N_1, N_2 \right) = S \left( N_1 \right) + S \left( N_2 \right) \). Thus, \( S \) must be an extensive quantity. This is a direct consequence of the principle of linear superposition as well as no self-diffusion hypothesis.

4 Some Consequences

If we confine to Clausius' definition of entropy change, then the phase space of thermodynamics becomes limited to systems having the same number of particles, i.e., only entropy difference can be calculated between two states having the same number of particles (in systems where \( N \) is not conserved, such as, black body radiation system, this limitation does not exist). But, since entropy is
extensive, entropy per particle \( s = \frac{S(N, p, T)}{N} \) will be a function of \( p \) and \( T \) alone and independent of \( N \). Hence, entropy changes can be calculated between states which differ in \( N \). This is clarified in the example discussed below.

Identical gases are confined in two chambers separated by a partition (Fig. 2). Temperature \( (T) \) in both chambers is the same but the pressure in one chamber is higher. If the partition is removed under adiabatic condition, the gas from the high pressure chamber will rush into the other chamber (i.e., from left to right) (Fig. 3). This is an adiabatic irreversible change and the total entropy is expected to increase.

The problem is how the increase in entropy can be demonstrated by actual calculation? For simplicity we assume the gas to be perfect. It is noted that, no external work is performed in this adiabatic process and hence \( \Delta W = \Delta Q = 0 \), i.e., internal energy \( (U) \) remains constant in the process. Hence, the final temperature, \( T_f = T \). Moreover, from the equation of state of a perfect gas, one can show that the final pressure, \( P_f = \frac{(p_1 + p_2)}{2} \). To calculate the change in entropy we have to connect the two states by a reversible path. This is done in two stages.

**Stage 1** — We put the whole system in thermal contact with a heat reservoir at a temperature \( T \). Then we remove the partition wall quasi-statically to the right so that the pressures in the two chambers are equal i.e., \( p_e \). In this process the increase in entropy will be:

\[
\Delta S = \frac{1}{T} \left[ \int p_1 dV + \int p_2 dV \right] \\
= \frac{V}{T} \left[ P_1 \ln \left( \frac{2P_1}{P_1 + P_2} \right) + P_2 \ln \left( \frac{2P_2}{P_1 + P_2} \right) \right] \quad \ldots (7)
\]

Here, the first term within the bracket is positive and the second term is negative. Since \( P_1 > P_2 \), \( \Delta S \) is a positive quantity.

**Stage 2** — Now the system is detached from the reservoir. The gases are in the two chambers whose volumes are unequal but the pressure and temperature are equal. To reach the final state we have to remove the partition wall. But will this process involve any change of entropy? We do not get an answer to this question from the existing principles of thermodynamics. According to our present postulate, (extensivity of entropy follows as a consequence of the present postulate in conjunction with the principle of linear superposition mentioned above) there is no change in entropy in stage 2. So that, total change in entropy will be given by Eq. (7). Thus adiabatic partition removal process in the present situation must be regarded as reversible, though, in general, partition removal process is irreversible. The above example shows the necessity of the extensivity of entropy in thermodynamics. Thus, the present investigation indicates a procedure by which two points in the larger thermodynamic phase space (which Landsberg' calls \( F \)) may be connected by a reversible path. As a result, entropy change can be calculated in all adiabatic irreversible processes. This may be stated to be the outcome of the present study.

It is well-known that, thermodynamics makes no assumption about the nature of the mechanics, the constituent atoms and molecules of a thermodynamic system satisfy. Classical statistical mechanics, however, leads to entropy expression, which is not strictly extensive. As such, it is inconsistent with thermodynamics. As the authors have already remarked, the principle of no self-diffusion effect already includes a feature which is true in quantum mechanics and violated in classical statistical mechanics. It is truly surprising that, even in the macroscopic thermodynamic systems, signature of subtle quantum concepts can be detected.

**References**


