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## On the derivation of $d'Q = T dS$

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**Abstract.** The traditional approach using Carnot cycles to the problem of establishing the existence of absolute temperature and entropy and to deriving  $d'Q = T dS$  is shown to remain valid for systems whose entropy is non-extensive as well as for systems whose entropy is extensive. However, it is seen that the analytical approach to this problem is valid only for systems whose entropy is extensive. Two methods for resolving this difficulty are presented.

### 1. Introduction

In a recent series of papers (Landsberg and Tranah 1980a, b, Tranah and Landsberg 1980), some of the thermodynamic properties of systems possessing non-extensive entropies were discussed. To a large extent, interest in such systems has been aroused by the fact that the entropy function for a black hole may be seen to be non-extensive (Smarr 1973, Hawking 1976). However, such systems are well known to astronomers, displaying as they do negative specific heats (see Lynden-Bell and Lynden-Bell 1977 and references cited therein).

Landsberg and Tranah considered, as an example of a non-extensive system, a generalised classical gas having entropy given, in terms of the independent variables  $V$ ,  $U$  and  $N$  (representing volume, internal energy and number of particles respectively), by

$$S = kN \ln(aUV^g/N^h)$$

where  $g, h > 0$  but  $h$  is not necessarily equal to  $(g + 1)$ . If two examples of such a gas are considered first as separate systems and then combined to form a composite system, the entropy,  $S$ , of the composite system is given by

$$S = S_1 + S_2 + \sigma \tag{1.1}$$

where the indices 1 and 2 refer to the two separate systems and

$$\sigma = kN_1 \ln(\gamma^h/\beta\alpha^g) + k(N - N_1) \ln[(1 - \gamma)^h/(1 - \beta)(1 - \alpha)^g].$$

Here  $\alpha = V_1/V$ ,  $\beta = U_1/U$ ,  $\gamma = N_1/N$  and it has been assumed that  $V = V_1 + V_2$ ,  $U = U_1 + U_2$ ,  $N = N_1 + N_2$ .

Therefore, for this system

$$S \geq S_1 + S_2,$$

equality holding only when  $\sigma = 0$ . Hence, in this case, the entropy is superadditive

rather than additive as would be the case if the entropy was extensive (Dunning-Davies 1983).

Again, it follows from (1.1) that

$$dS = dS_1 + dS_2 + d\sigma. \quad (1.2)$$

The form of (1.2) gives cause for concern when what might be termed the analytical approach to establishing the existence of absolute temperature and entropy (see Landsberg 1961) is considered, since this approach leads to the relation

$$dS = dS_1 + dS_2.$$

As is seen by comparing with (1.2), this latter equation does not hold for systems having non-extensive entropies. Therefore, as far as the analytical approach is concerned, the method for establishing the existence of absolute temperature and entropy—and, therefore, the method of deriving  $d'Q = T dS$ —needs to be examined since it is not valid generally. This will be done in § 2, where one method of resolving the difficulties encountered with this approach will also be presented.

Section 3 will be devoted to an examination of the more traditional approach to the derivation of  $d'Q = T dS$  in which use is made of Carnot cycles. It is found that this approach is valid for all systems irrespective of whether their entropies are extensive.

Finally, in § 4, an alternative way of resolving the difficulties encountered with the analytical approach will be presented.

## 2. Analytical approach to the derivation of $d'Q = T dS$

This approach consists of two steps:

(1) the second law of thermodynamics is used to show that the increment of heat,  $d'Q$ , possesses an integrating factor;

(2) the derivation is completed by considering the thermal equilibrium of two systems; applying the result that an integrating factor exists to each system separately and also to the combined system; and using

$$d'Q = d'Q_1 + d'Q_2 \quad (2.1)$$

for the increment of heat supplied to the combined system by quasi-static processes.

This latter point is violated for a non-extensive system since, in that case, if increments of heat  $d'Q_1$  and  $d'Q_2$  are given to the two separate systems, the increment of heat  $d'Q$  given to the composite system would not be given by (2.1) but rather by

$$d'Q = d'Q_1 + d'Q_2 + d'q \quad (2.2)$$

where  $d'q$  might be termed an increment of 'heat of interaction' and would be zero only for an extensive system.

Again, in this approach, all the systems to be considered are supposed to be simple systems. As has been pointed out by Münster (1970), this means that the composite system and each separate system on its own should constitute a closed system. Since (2.2), rather than (2.1), holds for a non-extensive system, this latter point is violated also for such a system.

However, when the two separate systems are regarded as parts of a composite system, the total amount of heat given specifically to the two systems is  $(d'Q_1 + d'Q_2)$ ,

although the composite system itself received an amount of heat  $d'Q$  given by (2.2). This quantity of heat ( $d'Q_1 + d'Q_2$ ), which will be denoted by  $d'\Phi$ , is the total amount of heat which would have been given to the composite system if it had been extensive or, alternatively, if all the systems under consideration had been simple. Hence, consider

$$d'\Phi = d'Q_1 + d'Q_2.$$

By using the usual methods adopted in the analytical approach, it may be shown that quantities  $\Sigma$ ,  $S_1$ ,  $S_2$  and  $T$  exist such that

$$d'Q_1 = T dS_1 \quad d'Q_2 = T dS_2,$$

and

$$d'\Phi = T d\Sigma.$$

Again, the total increment of heat actually given to the composite system is  $d'Q$ . If this composite system is supposed placed in thermal contact with some other system and these are regarded as two separate systems then, by repeating the above argument, it may be shown that a quantity  $S$  exists such that

$$d'Q = T dS.$$

Hence, it follows from (2.2) that

$$T d\Sigma = d'\Phi = d'Q - d'q = T dS - d'q$$

or

$$dS - d\Sigma = T^{-1}d'q = d\sigma;$$

that is,  $d'q$  has an integrating factor.

Therefore, in thermal equilibrium

$$d'Q = d'Q_1 + d'Q_2 + d'q$$

implies

$$T dS = T dS_1 + T dS_2 + T d\sigma$$

and, once again, it is concluded that  $d'Q = T dS$ . In this modified analytical approach, it is assumed nowhere (either directly or indirectly) that the entropy is extensive.

### 3. The traditional derivation of $d'Q = T dS$

The well known traditional approach to the derivation of  $d'Q = T dS$  may be split up quite conveniently into four parts. By assuming the validity of the second law of thermodynamics, it is necessary to prove that

(a) if a system is taken around a reversible cycle, absorbing heat  $Q_1$  at temperature  $\theta_1$  and heat  $Q_2$  at temperature  $\theta_2$ , the ratio  $Q_1/Q_2$  is a function of  $\theta_1$  and  $\theta_2$  only;

(b) this ratio may be written

$$Q_1/Q_2 = T_1/T_2$$

where  $T_1$  and  $T_2$  are absolute temperatures;

(c) the entropy,  $S$ , defined by

$$dS = (d'Q/T)_{\text{rev}}$$

is a function of state;

(d) for an adiabatically isolated system, the entropy never decreases.

Following Denbigh (1971), it is seen that, to prove (a), it is necessary first to show that  $Q_1$  and  $Q_2$  must have opposite signs. To complete the proof, two systems are considered and both are taken around the same cycle. If the second system absorbs heat  $Q'_1$  and  $Q'_2$  at temperatures  $\theta_1$  and  $\theta_2$  respectively, the proof depends on finding integers  $n$  and  $n'$  such that, if the first system is taken through  $n$  complete cycles and the second through  $n'$  complete cycles in the opposite direction, then

$$nQ_1 = -n'Q'_1. \quad (3.1)$$

The term  $nQ_1$  is obtained by giving an amount of heat  $Q_1$  to the first system in each of the  $n$  cycles and so, the difficulties encountered in § 2, when discussing the composite system, do not occur. A similar comment applies for the term  $n'Q'_1$  also. Hence nowhere in the argument do questions of extensivity arise and so, the proof of (a) holds for all systems.

As far as the proof of (b) is concerned, it is seen (Thompson 1972) that it is necessary to consider one system only and questions of extensivity simply do not arise. Hence, this proof holds for all systems.

To prove (c), it is necessary to consider any arbitrary closed reversible cycle approximated by a network of Carnot cycles (Denbigh 1971, Thompson 1972). Suppose that, in the  $i$ th of these cycles, quantities of heat  $\delta'Q_{ih}$  and  $\delta'Q_{ic}$  are absorbed at temperatures  $T_{ih}$  and  $T_{ic}$  respectively. Then, for this cycle

$$\delta'Q_{ih}/T_{ih} + \delta'Q_{ic}/T_{ic} = 0.$$

Such an equation will exist for each cycle of the network and adding together as many of these equations as the number of Carnot cycles into which the actual cycle has been divided gives

$$\sum_i \left( \frac{\delta'Q_{ih}}{T_{ih}} + \frac{\delta'Q_{ic}}{T_{ic}} \right) = 0.$$

Due to the way in which this result is obtained, the problems met in § 2, when discussing the composite system, do not arise. Also, since each individual contribution to this sum is of the form  $\delta'Q_j/T_j$ , this latter equation may be written

$$\sum_j \left( \frac{\delta'Q_j}{T_j} \right) = 0.$$

If the network is allowed to become finer and finer, Carnot's theorem that, for any closed reversible cycle  $C$ ,

$$\oint_C \frac{\delta'Q}{T} = 0$$

is seen to follow in the limit.

Hence, the proof of (c) also holds for all systems since, once again, questions of extensivity simply do not arise in the proof. However, although they will be seen to have no effect on the proof of (c), two further points might be noted at this juncture.

Firstly, suppose a system consists of  $n$  parts, each at the same temperature  $T$ . If the various parts absorb quantities of heat  $d'Q_1, d'Q_2, \dots, d'Q_n$  under reversible conditions, their entropy changes are

$$d'Q_1/T, \quad d'Q_2/T, \quad \dots, \quad d'Q_n/T$$

respectively. The sum of these is  $(\sum_i d'Q_i)/T$ . Also, if  $d'Q$  is the total amount of heat absorbed by the whole system, it will equal  $\sum_i d'Q_i$  only if the system is extensive. In general

$$d'Q = \sum_i d'Q_i + d'q \geq \sum_i d'Q_i.$$

Hence, the sum of the entropy changes of the various parts will be less than or equal to the overall entropy change, equality holding when the system under consideration is extensive.

Secondly, if a system consisting of  $n$  parts is taken around a cycle in which quantities of heat  $Q_h$  and  $Q_c$  are absorbed from reservoirs at temperatures  $T_h$  and  $T_c$  respectively, then

$$Q_h/T_h + Q_c/T_c = 0. \tag{3.2}$$

If the individual parts absorb amounts of heat  $Q_{ih}$  and  $Q_{ic}$  ( $i = 1, 2, \dots, n$ ) from the reservoirs at temperatures  $T_h$  and  $T_c$  respectively,

$$Q_{ih}/T_h + Q_{ic}/T_c = 0 \tag{3.3}$$

for  $i = 1, 2, \dots, n$ .

However, in general,

$$Q_h = \sum_i Q_{ih} + q_h \geq \sum_i Q_{ih}$$

and

$$Q_c = \sum_i Q_{ic} + q_c \geq \sum_i Q_{ic},$$

equality holding only when an extensive system is under consideration.

Hence,

$$\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = \sum_i \left( \frac{Q_{ih}}{T_h} + \frac{Q_{ic}}{T_c} \right) + \frac{q_h}{T_h} + \frac{q_c}{T_c}.$$

Using (3.2) and (3.3), it follows that

$$q_h/T_h + q_c/T_c = 0$$

that is, what might be termed the total 'entropy of interaction' in the cycle is also zero.

Therefore, if a system consisting of  $n$  parts is under consideration, it is seen that the quantities  $Q_h$  and  $Q_c$ , rather than  $Q_{ih}$  and  $Q_{ic}$  ( $i = 1, 2, \dots, n$ ), are of importance when calculating the efficiency. However, by the nature of the arguments, these considerations are seen to have no effect on the validity of the proof of (c).

The proof of (d) is seen to hold for all systems since, once again, questions of extensivity do not arise in it (Thompson 1972).

It might be noted that the difficulties which may arise, due to non-extensivity, when considering the giving of heat to a system, occur only when composite systems (as in § 2) or the separate parts of a particular system (as considered earlier in this

section) are under consideration. No such difficulties occur when the giving of heat to a single system is under consideration. Hence, for example, no such difficulties arise in the derivation of (3.1).

Therefore, the traditional approach using Carnot cycles is seen to lead to the existence of absolute temperature and entropy, as well as to the derivation of  $d'Q = T dS$ , without assuming—either directly or indirectly—that the entropy is extensive.

#### 4. An alternative resolution of the problem

To some, one of the appeals of the analytical approach to thermodynamics is that it is totally divorced from heat cycles and other concepts borrowed from engineering. However, a combination of the analytical and traditional approaches offers an alternative resolution of the problem discussed in § 2.

By the usual analytical methods, it may be deduced using the second law as starting point, that the increment of heat  $d'Q$  possesses an integrating factor; that is

$$d'Q = \lambda d\phi \quad (4.1)$$

where  $\lambda \equiv \lambda(t, \phi, a_3, a_4, \dots)$  and the independent thermodynamic variables are the empirical temperature  $t$ , the empirical entropy  $\phi$ , and other variables  $a_3, a_4, \dots$  (Landsberg 1961).

Now, if a system is taken around a reversible cycle, absorbing heat  $d'Q_1$  at temperature  $t_1$  and heat  $d'Q_2$  at temperature  $t_2$ , then, as mentioned in § 3, it may be shown that

$$d'Q_2/d'Q_1 = \theta(t_2)/\theta(t_1)$$

where  $\theta$  is some function of  $t$  alone.

But, applying (4.1) to each of the increments of heat  $d'Q_1$  and  $d'Q_2$  leads to the alternative expression

$$d'Q_2/d'Q_1 = \lambda(t_2, \phi, a_3, a_4, \dots) d\phi / \lambda(t_1, \phi, a_3, a_4, \dots) d\phi.$$

For the latter two equations to be satisfied, it is necessary that

$$\lambda(t, \phi, a_3, a_4, \dots) = \theta(t)\Phi(\phi, a_3, a_4, \dots).$$

Under these conditions

$$d'Q = \lambda d\phi = T dS$$

where, if  $c$  is some constant,

$$T = c\theta(t), \quad dS = c^{-1}\Phi(\phi, a_3, a_4, \dots) d\phi.$$

Again in this alternative discussion of the problem of establishing the existence of absolute temperature and entropy and of deriving  $d'Q = T dS$ , extensivity of the system has been assumed nowhere.

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