

ON THE MEANING OF EXTENSIVITY

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It is shown that the various definitions of an extensive quantity appearing in the standard thermodynamics texts are not equivalent. Furthermore, none of these is found to be equivalent to the usual statistical-mechanical meaning. It is proposed that the statistical-mechanical meaning of an extensive quantity be adopted as the universal definition.

1. Introduction. In statistical mechanics, it seems quite clear what is meant by an extensive quantity. For example, for fixed T and for large N and V with fixed density $\rho = N/V$, the entropy is extensive if

$$S(V, N, T) \sim Ns(\rho, T),$$

or, more accurately, the limit

$$\lim_{\substack{N, V \rightarrow \infty \\ \rho \text{ fixed}}} \frac{1}{N} S(V, N, T) = s(\rho, T)$$

exists and depends on the intensive quantities ρ and T only. Here intensive quantities are those which are independent of the size of the system [1].

However, in thermodynamics, the position is not quite so clear-cut. Several definitions of extensive appear in the standard texts and close examination shows that these are not equivalent to one another or to the statistical-mechanical definition given above. In fact, in thermodynamics texts, extensive quantities are defined variously as:

(1) Those quantities whose values in a composite system equal the sum of the values in each of the subsystems [2,3].

(2) Those quantities whose values are halved when a system in equilibrium is divided into two equal parts [4].

(3) Those quantities which are homogeneous of degree one [5].

It is proposed to examine the way in which these various definitions are related to one another and

hopefully to conclude which would seem to be the most sensible and useful to adopt as the standard definition of an extensive quantity.

2. Extensivity. Consider some quantity f which is supposed to be dependent on the three independent variables x, y and z . If $f \equiv f(x, y, z)$ is assumed extensive in the sense of definition (1) of section 1, then

$$\begin{aligned} f(x_1 + x_2, y_1 + y_2, z_1 + z_2) \\ = f(x_1, y_1, z_1) + f(x_2, y_2, z_2), \end{aligned} \quad (1)$$

where (x_1, y_1, z_1) and (x_2, y_2, z_2) are the values of the independent variables in two subsystems.

If the two subsystems are identical so that $x_1 = x_2$, $y_1 = y_2$, $z_1 = z_2$, this relation leads to

$$f(2x_1, 2y_1, 2z_1) = 2f(x_1, y_1, z_1)$$

and so, definition (1) does imply definition (2).

Again, if a system which is composed of n identical subsystems is considered, eq. (1) yields

$$f(nx, ny, nz) = nf(x, y, z), \quad (2)$$

where n is an integer.

By putting $nx = X$, $ny = Y$, $nz = Z$, this latter equation implies that

$$n^{-1}f(X, Y, Z) = f(n^{-1}X, n^{-1}Y, n^{-1}Z).$$

Validity of eq. (2) for rational numbers m/n follows by noting that

$$f(mn^{-1}x, mn^{-1}y, mn^{-1}z) = mf(n^{-1}x, n^{-1}y, n^{-1}z) = mn^{-1}f(x, y, z).$$

∴ Provided $f(x, y, z)$ is a continuous function, definition (1) is seen to imply definition (3). Also, the same argument shows that, provided $f(x, y, z)$ is continuous, definition (2) implies definition (3).

If $f \equiv f(x, y, z)$ is assumed extensive in the sense of definition (3) of section 1, then

$$f(ax, ay, az) = af(x, y, z).$$

By taking $a = 2$, it is obvious immediately that definition (2) is implied by definition (3). Hence, these two definitions are not quite equivalent due to the proviso regarding continuity which must be imposed before definition (3) may be deduced from definition (2).

Possibly the most straightforward way of showing that neither definition (3) nor definition (2) implies definition (1) is to consider the following example:

For an ideal classical gas, the entropy is proportional to

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

where $g, h > 0$ and $h = g + 1$ [5]. Here U is the internal energy, V the volume and N the number of particles.

This entropy is seen to be an extensive quantity as judged by definitions (2) and (3). However, if two systems together with the composite system formed from them are considered, it is seen that

$$\begin{aligned} & S(U_1 + U_2, V_1 + V_2, N_1 + N_2) \\ & - S(U_1, V_1, N_1) - S(U_2, V_2, N_2) \\ & = kN \ln \{ [(1 - \gamma)^h / (1 - \alpha)(1 - \beta)^g]^{1-\gamma} (\gamma^h / \alpha\beta^g)^\gamma \}, \end{aligned} \tag{3}$$

where $\alpha = U_1 / (U_1 + U_2)$, $\beta = V_1 / (V_1 + V_2)$, $\gamma = N_1 / (N_1 + N_2)$. The quantity on the right-hand side of eq. (3) is zero only if $\alpha = \beta = \gamma$. Hence, for this example, the entropy is additive, and, therefore, extensive as judged by definition (1), only if the added condition $\alpha = \beta = \gamma$ is imposed.

Hence, the assertion that the three forms of the definition of an extensive quantity found in thermodynamics textbooks are not equivalent is seen to be true. Also, since the statistical-mechanical definition is seen

to imply that an extensive quantity is both additive and homogeneous of degree one, it follows that none of the thermodynamic definitions is equivalent to the statistical-mechanics one.

However, it might be noted that, if the entropy S is homogeneous of degree one, then

$$S(aU, aV, aN) = aS(U, V, N), \tag{4}$$

where U is internal energy, V volume and N number of particles.

Additivity of the entropy,

$$\begin{aligned} & S(U_1 + U_2, V_1 + V_2, N_1 + N_2) \\ & = S(U_1, V_1, N_1) + S(U_2, V_2, N_2), \end{aligned}$$

is implied only if

$$U_2 = xU_1, \quad V_2 = xV_1, \quad N_2 = xN_1.$$

Hence, if $U = Nu$ and $V = Nv$, where u and v are respectively the internal energy and volume per particle, and S is homogeneous of degree one, then S is extensive in the statistical mechanical sense; that is,

$$S(U, V, N) = Ns(u, v),$$

where $s(u, v)$ depends only on the internal energy and volume per particle and is seen to be the entropy per particle.

A further point which should be noted is that, if the entropy is defined to be an extensive quantity according to the statistical-mechanics definition, it is seen that the conditions of the implicit-function theorem are satisfied [6] and eq. (4) may be inverted to give, for example, U as a function of S, V and N . In the past, the conditions under which this could be done have been alluded to but not stated explicitly [5].

In conclusion, it would appear that the most sensible definition to adopt for an extensive quantity is that which currently appears in statistical-mechanics texts. This proposal is advanced since extensive quantities so defined would possess all the properties listed here as the thermodynamic definitions (1), (2) and (3) and, although not stated explicitly, this definition is implied occasionally in thermodynamics literature already [7].

References

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