A method to illustrate the extensive and intensive properties of thermodynamic variables

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INTRODUCTION

Over the last ten years, unified courses in thermal physics, including both macroscopic thermodynamics and microscopic statistical mechanics, have become increasingly common, particularly at the undergraduate level. This reflects a change from traditional curricula, where entire courses are devoted to classical thermodynamics and statistical physics is briefly introduced in survey courses in modern physics, with serious study delayed until graduate school. A thorough understanding of statistical and probabilistic is becoming increasingly important to chemists and physicists. This understanding is often developed by a serious study of statistical mechanics. Undergraduate thermal physics provides an ideal foundation for such study.

Undergraduate courses in thermal physics do not afford us the time follow the languid, historical, phenomenological development of the laws of thermodynamics as exemplified in the classic text by Zemansky (1981). The study of thermodynamics can be abbreviated by using the axiomatic method. The most widely accepted axioms are those proposed by Callen (1960). A thorough discussion of these axioms is provided in Callen's *Thermodynamics* and in the more recent book by Tien and Lienhard (1985). In the axiomatic approach, the extensive or intensive nature of thermodynamic variables is emphasized and the relationship to the theory of homogeneous functions is presented. However, this relationship is not often exploited, and an opportunity to provide a foundation for the later study of critical point phenomena is lost.

In the following sections the relationship between homogeneous function theory and thermodynamics is developed, and, as an illustration, a method for calculating the thermodynamic properties of N moles of a material if an equation is known for a fixed amount of that material. The author first became familiar with some of these methods in a course based on Callen's text, and began to use them some years later after having developed a course in thermal physics. An extended literature search has failed to find a description of the methods described herein.

HOMOGENEOUS FUNCTIONS

As the properties of homogeneous functions are not well known, they are reviewed here. As is well known, a polynomial of the form

$$A_0 + A_1 x + A_2 x^2 + \ldots + A_n x^n \quad \textbf{(1)}$$

is of degree *n,* if A_n is not equal to zero. Thus, the degree of a polynomial is equal to the largest exponent in the polynomial. A polynomial in more than one variable is said to be *homogeneous* if all of its terms are of the same degree. For example, the polynomial in variables x and y

$$f(x,y) = x^2 + 2xy + y^2 \qquad \textbf{(2)}$$

is homogeneous of degree *2*. This much is familiar.

The property of homogeneity can be extended to more general functions. We shall consider general functions that are homogeneous in terms of functional equations. The functional equations appropriate to the study of homogeneous functions were developed by Euler (1755, 1768, 1770). Aczel (1966, 1969), Davis (1962), Stanley (1970), and Widder (1961) provide modern introductions with varying degrees of sophistication to the subject of functional equations.

In general, a function $f(x)$ is a homogeneous function if for all values of the parameter λ,

$$f(\lambda x) = g(\lambda) f(x) \qquad \textbf{(3)}$$

The function g is usually called the scaling function in thermodynamics. The function g is not an arbitrary function, it is given by $g(\lambda) = \lambda^n$, see Stanley (1971). Thus a homogeneous function $f(x)$ is one that satisfies

$$f(x\lambda) = \lambda^n f(x) \qquad \textbf{(4)}$$

This definition can be extended to any finite number of variables. In elementary thermodynamics we are usually interested in functions that are homogeneous of degree zero or one. It is possible for multidimensional functions to be homogeneous in different degrees for the different variables. This is common occurrence in thermodynamics. For a function in the variables x, y, and z; the function

$$f(\lambda x, \lambda y, z) = \lambda^n f(x,y,z) \qquad \textbf{(5)}$$

then we say that this function is homogeneous of degree n in x and y and that it is not homogeneous in z.

A generalization, described by Stanley (1971), is that of a *generalized homogeneous function.* Generalized homogeneous functions are those that satisfy

$$f(\lambda^a x, \lambda^b y) = \lambda f(x,y). \qquad \textbf{(6)}$$

It is this formulation that is widely used in the analysis of critical point phenomena and phase transitions using the static scaling hypothesis.

For clarity in the following presentation, functions homogeneous of degree zero and one are treated separately. The reader will readily observe that a single theorem, true for any *n*, could have been presented. The method of proof for the general theorem is a straightforward extension of the proof of Theorem 1 presented below. The author has found that an initial presentation of separate theorems is preferred by most physics students. The general theorem is assigned as a homework problem, and is used by mathematically oriented students.

In thermodynamics, variables are classified as either *extensive* or *intensive*. Extensive variables are those that vary linearly with the size of the system. Internal energy, E, is an example of an extensive variable. Extensive variables exhibit the property of being additive over a set of subsystems. As example: if a system is composed two subsystems, one with energy E_1, the second with energy E_2, then the total system energy is $E = E_1 + E_2$. Other examples of extensive variables in thermodynamics are: volume, V, mole number, N, entropy, S, enthalpy, H, Helmholtz free energy, F, and the Gibbs free energy, G.

Other thermodynamic variables are independent of the size of the system , these variables are referred to as *intensive* variables. The intensive variables commonly encountered in thermodynamics are temperature, T, pressure, p, and the *chemical potential* of the i^{th} component of the system, μ_i.

THE RELATIONSHIP BETWEEN HOMOGENEOUS FUNCTIONS AND EXTENSIVE AND INTENSIVE VARIABLES

Entropy, which is usually an extensive variable in thermodynamics, can be expressed as a function of three other extensive variables: internal energy, volume, and number of moles. (Entropy is not always extensive, there are exceptions – see Hill (1962), Landsberg (1978), or Robertson (1993) for examples.) Thus, we can write entropy as $S = S(E,V,N)$. An equation of this form contains complete thermodynamic information, it is called the *fundamental relation* in thermodynamics. Since extensive variables depend on the size of the system, they can be represented by homogeneous, first degree functions. Given the fundamental relation for entropy, we can write

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N). \qquad \textbf{(7)}$$

The scaling function λ is arbitrary, and following Callen (1960) we choose $\lambda = 1/N$. The entropy equation can be rewritten as

$$S(\frac{E}{N},\frac{V}{N},1)=\frac{1}{N}S(E,V,N). \qquad \textbf{(8)}$$

Next, we introduce the internal energy per mole as $e = E/N$, and the volume per mole $v=V/N$, then

$$S(e,v,1)=s(e,v)=\frac{1}{N}S(E,V,N) \qquad \textbf{(9)}$$

or

$$Ns(e,v)=S(E,V,N) \qquad \textbf{(10)}$$

where $s(e,v)$ is the entropy per mole. This tells us that the entropy of N moles of a substance is N times the entropy per mole of that substance. The result is well known, the method used to derive it can be generalized to provide a result of more general usefulness.

The intensive functions of thermodynamics are homogeneous functions of degree zero of the extensive variables. Callen (1960) has shown that the intensive parameters of a thermodynamic system can be written as functions of the extensive variables; that is $T = T(S,V,N)$, $P = P(S,V,N)$, and $\mu = \mu(S,V,N)$. These expressions are called *equations of state*. Each of these functions is homogeneous of degree zero in the specified variables, this follows as each of these can be expressed as a first partial derivative of the energy or entropy of the system. The details can be found in Chandler (1987). For example, the temperature function $T = T(S,V,N)$ obeys

$$T(\lambda S,\lambda V,\lambda N)=T(S,V,N). \qquad \textbf{(11)}$$

This means that in a composite system in thermal equilibrium, the temperature in any sub-subsystem is equal to the temperature of the system.

THEOREMS ON INTENSIVE AND EXTENSIVE FUNCTIONS

We now establish theorems for intensive and extensive functions and then discuss some of their thermodynamic applications.

THEOREM 1 (Extensive Functions): Consider a function $f(x,y,z)$, homogeneous of degree one in the variables y and z, . Let one of the homogeneous variables be a non-zero constant, $z = z_0$, then we can write $f(x,y,z_0) = g(x,y)$. Then

$$f(x,y,z) = \frac{z}{z_0} g(x, y\frac{z_0}{z}) . \quad \textbf{(12)}$$

PROOF: Write $f(x,y,z)$ as

$$f(x,y,z) = \frac{z}{z_0}\frac{z_0}{z} f(x,y,z) . \quad \textbf{(13)}$$

Then, by choosing $\lambda = z_0/z$, we can rewrite (13), using the fact it is homogeneous in the variables y and z, so we have

$$f(x,y,z) = \frac{z}{z_0} f(x, y\frac{z_0}{z}, z\frac{z_0}{z}) = \frac{z}{z_0} f(x, y\frac{z_0}{z}, z_0) \quad \textbf{(14)}$$

Now, since z_0 is a constant, we can write (14) as

$$f(x, y\frac{z_0}{z}, z_0) = g(x, y\frac{z_0}{z}) , \quad \textbf{(15)}$$

thus, we have

$$f(x,y,z) = \frac{z}{z_0} g(x, y\frac{z_0}{z}) \quad \textbf{(16)}$$

which completes the proof.

THEOREM 2 (Intensive Functions) : Consider a function $f(x,y,z)$, that is homogeneous degree zero in the variables y and z. Let one of the homogeneous variables be a non-zero constant, $z = z_0$, then we can write $f(x,y,z_0) = h(x,y)$. Then

$$f(x,y,z) = h(x, y\frac{z_o}{z}) . \quad \textbf{(17)}$$

PROOF: Since in this case $f(x, \lambda y, \lambda z) = \lambda^0 f(x,y,z) = f(x,y,z)$, choosing $\lambda = z_0/z$, we can write $f(x,y,z)$ as

$$f(x, y\frac{z_0}{z}, z_0) = f(x,y,z) \quad \textbf{(18)}$$

then

$$h(x, y\frac{z_0}{z}) = f(x, y, z) \qquad \textbf{(19)}$$

which is the theorem.

APPLICATIONS

We will now consider some illustrations of these theorems. Given that the internal energy of a system for three moles of a substance is $E = pV^2$, what is the internal energy for N moles? We want $E(p, V, N)$, using Theorem 1, we can write

$$E(p, V, N) = \frac{N}{N_0} g(p, V\frac{N_0}{N}), \qquad \textbf{(20)}$$

where $g(p,v) = pV^2$, and $N_0 = 3$. Thus,

$$E(p, V, N) = \frac{N}{3}(P(\frac{3V}{N})^2) = 3\frac{pV^2}{N}. \qquad \textbf{(21)}$$

As a second illustration of Theorem 1, consider the entropy of one mole of some substance described by the equation

$$s = R\ln\left(E^{3/2}V\right) + C, \qquad \textbf{(22)}$$

where C is a constant and R is the ideal gas constant. To determine the entropy for N moles of this material, we use from Theorem 1 to write (22) as

$$S = \frac{N}{N_0}\left\{R\ln\left(\left(\frac{EN_0}{N}\right)^{3/2}\frac{VN_0}{N}\right) + C\right\}, \qquad \textbf{(23)}$$

but $N_0 = 1$, so

$$S = NR\ln\left(E^{3/2}VN^{-5/2}\right) + NC. \qquad \textbf{(24)}$$

Many similar results could be proved, but these are sufficient to illustrate Theorem 1.

We now illustrate Theorem 2. Again, let the number of moles, N play the role of the coordinate z so that $z_o = N_0$. The van der Waals equation of state for a single mole of gas is

$$p = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{25}$$

where *a* and *b* are phenomenological constants. We use Theorem 2 to find the equation of state for *N* moles. Applying the theorem, we write

$$p(T,V,N) = p(T, V\frac{N_0}{N}), \tag{26}$$

so the pressure for *N* moles is

$$p = \frac{RT}{\frac{V}{N} - b} - \frac{a}{\left(V/N\right)^2} = \frac{NRT}{V - Nb} - \frac{N^2 a}{V^2}, \tag{27}$$

which is, of course, the van der Waals equation for *N* moles.

DISCUSSION AND CONCLUSIONS

The usefulness of homogeneous functions in thermodynamics has been demonstrated. The use of the theorems presented above circumvents the common tendency of students to scale thermodynamic results incorrectly, and provides a deeper insight into the meaning of the extensivity of entropy. The theorems presented above also provide a deeper understanding of the relationship between the fundamental relation of thermodynamics and the equations of state.

The methods of functional equations are extremely useful in the analysis of critical point phenomena, and while not well known, they can, and have been applied to other sub-fields of physics. Some examples are the application to relativity Lunn (1919), to communication theory by Shannon (1948), and to information theory by Jaynes (1957). These applications to a number of different fields indicate that physicists would benefit from greater familiarity with functional equations. The theorems derived in this paper are useful for calculating general results from measurements made on fixed amounts of materials. The methods presented also enable students to develop an understanding of the mathematical techniques used in the application of homogeneous functions in simple situations; this allows these students to concentrate on physics when they meet critical point phenomena, thus affording a deeper understanding.

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