Journal of the Arkansas Academy of Science

Volume 45 Article 35

1991

Homogenous Functions in Thermodynamics

Stephen R. Addison
University of Central Arkansas

Recommended Citation

Addison, Stephen R. (1991) "Homogenous Functions in Thermodynamics," *Journal of the Arkansas Academy of Science*: Vol. 45 , Article 35.
Available at: http://scholarworks.uark.edu/jaas/vol45/iss1/35

GENERAL NOTES

HOMOGENOUS FUNCTIONS IN THERMODYNAMICS

Historically, the laws of thermodynamics were developed using phenomenological methods; the statements of these laws, and of the results deduced from them, were framed in terms of macroscopic mechanical systems. The teaching of thermodynamics has traditionally followed this historical, phenomenonological approach. This approach is exemplified by the classic book by Zemansky and Dittman (1981). Traditional courses in thermodynamics have followed this historical development and have, as a result, been devoted to purely macroscopic concepts.

The microscopic science of statistical mechanics has largely been developed in this century and until recently it was covered in a separate course. In recent years it has become increasingly common to treat macroscopic thermodynamics and microscopic statistical mechanics in a single course, this course is usually called thermal physics. This means that the traditional, languid introduction to macroscopic thermodynamics can no longer be used and a different approach is needed. The study of thermodynamics can be shortened by using a system of axioms instead of the phenomenonological approach.

Several attempts have been made to provide thermodynamics with an axiomatic basis, the most widely used system of axioms was developed by Callen (1960). This paper will not explicitly deal with these axioms, the interested reader is referred to the book by Callen or to the more recent book by Tien and Lienhard (1985). In the axiomatic approach to thermodynamics, the question of whether a thermodynamic variable is *extensive* or *intensive* is emphasized. This paper concentrates on the relationship between homogenous function theory and extensive and intensive thermodynamic variables, and it develops a method of calculating the thermodynamic properties of N moles of a material if an equation is known for some fixed amount of that material.

HOMOGENEOUS FUNCTIONS

As the properties of homogeneous functions are not well known, their major properties are presented in detail in this section.

We shall consider functions which are homogenous 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 (1960), Stanley (1971), and Widder (1961) provide modern introductions, of varying degrees of sophistication, to the subject of functional equations.

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

$$f(\lambda x) = g(\lambda) f(x).$$

Where the function g(l) is usually called the scaling function in thermodynamics. Stanley (1971) has shown at the function g(l) is not an arbitrary function, instead g(l) is given by

$$g(\lambda) = \lambda^n.$$

Thus, a homogeneous function f(x) of degree n is a function in which

$$f(\lambda x) = \lambda^n f(x).$$

This definition can be generalized to any finite number of variables. The degree n can take on any value – positive, negative or zero. It is possible for functions to be homogeneous of different degree in different variables. This is true of some of the functions which occur in thermodynamics.

If we have a function of the variables *x*, *y* and *z*, f(x,y,z), and if for this function,

$$f(x, \lambda y, \lambda z) = \lambda^n f(x,y,z),$$

then we say that this function is homogeneous of degree *n* in e variables y and *z*.

The idea of homogeneous functions admits further generalization (Stanley, 1971); a function f(x,y) is called a generalized homogeneous function if

$$f(\lambda^a x, \lambda^b y) = \lambda f(x,y).$$

It is this generalized formulation that is used in the analysis of critical point phenomena and phase transitions using the static scaling hypothesis. The reader should note that

$$f(\lambda^a x, \lambda^b y) = \lambda^p f(x,y)$$

is not a further generalization. This is clear since, by choosing $\lambda^p = \Lambda$ we can rewrite the equation as

$$(\Lambda^{a/p} x, \Lambda^{a/p} y) = \Lambda f(x,y).$$

We can now choose p = 1 without loss of generality and observe that this form is equivalent to the original definition of a generalized homogeneous function.

In the rest of this paper I will restrict my attention to functions which are homogeneous of degree zero or order one. It is these simpler cases that are useful in elementary thermodynamics.

EXTENSIVE AND INTENSIVE THERMODYNAMIC VARIABLES

The variables which occur in thermodynamics are either *extensive* or *intensive*.

The internal energy (E) of a thermodynamic system is an example of an extensive variable. If a variable is described as *extensive* then that variable depends linearly on the size of the system. In other words, if a system is composed of several sub-systems, the value of the extensive quantity for the composite system is calculated by summing over the sub-systems. As an example, if a system is composed of a sub-system of internal energy E_1, and a second sub-system of energy E_2, then the energy of the composite system is $E = E_1 + E_2$. We may state this property succinctly by stating that *extensive quantities are additive over a set of sub-systems*. Other extensive variables that occur in thermodynamics are: volume (V), mole number (N), entropy (S), enthalpy (H), Helmholtz free energy (F), and Gibbs free energy (G).

Some variables that occur in thermodynamics are independent of the size of the system, these variables are called *intensive* variables. The intensive variables of 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 an extensive variable, can be expressed as a function of three other extensive variables: internal energy, volume and number of moles. That is we may write S=S (E,V,N). An equation of this form contains complete thermodynamic information, it is called the *fundamental relation* in thermodynamics. Now, we have stated that extensive variables depend linearly on the size of the system, this means that extensive variables can be represented by homogeneous first degree functions. Thus, given S=S (E,V,N) we can immediately write

$$S(\lambda E,\lambda V,\lambda N) = \lambda S(E,V,N).$$

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

$$S\left(\frac{E}{N},\frac{V}{N},1\right)=\frac{1}{N}S(E,V,N).$$

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

$$S(e,v,1) = s(e,v) = 1/N\ S(E,V,N)$$

or

$$N\ s(e,v) = S(E,V,N),$$

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. This result is well known, the method by which it was arrived at can be generalized to provide a result of more general utility. This will be done in the next section, first we will further investigate intensive functions.

The intensive functions of thermodynamics are homogeneous functions of order zero of the extensive variables. Callen (1960) shows that the intensive parameters of a thermodynamic system may be written as functions of the extensive variables in the following manner:

$$T = T(S,V,N)$$

$$P = P(S,V,N)$$

$$\mu = \mu(S,V,N).$$

These expressions for the intensive variable in rms of extensive variables are called *equations of state*. Each of these functions is homogeneous of degree zero, 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). We will consider temperature as an example, for the temperature function T(S,V,N),

$$T(\lambda S,\lambda V,\lambda N) = T(S,V,N).$$

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

THEOREM

Consider a function f(x,y,x) that is homogeneous of degree n in the variables y and z. That is,

$$f(x,\lambda y,\lambda z) = \lambda^n f(x,y,z).$$

Now if we let $z = z_o$, we may write

$$f(x,y,z_o) = g(x,y),$$

where g(x,y) is the value of f(x,y,z) at Z = Zo.
Then

$$f(x,y,z)=\left(\frac{Z}{Z_o}\right)^n g\left(x,y\frac{Z_o}{Z}\right),$$

where Z and Zo are non-zero.
This result can be proved as follows. First we write f(x,y,z) as

$$f(x,y,z) = \left(\frac{Z}{Z_o}\right)^n\left(\frac{Z_o}{Z}\right)^n f(x,y,z).$$

By choosing $\lambda = z_o/z$ we can rewrite this equation using the fact that it is homogeneous of degree one in the variables y and z, so we have

$$f(x,y,z)=\left(\frac{Z}{Z_o}\right)^n f\left(x,y\frac{Z_o}{Z},Z\frac{Z_o}{Z}\right)=\left(\frac{Z}{Z_o}\right)^n f\left(x,y\frac{Z_o}{Z},Z_o\right).$$

Now, Zo is a constant so clearly we may write

$$f\left(x, y\frac{Z_o}{Z}, Z_o\right) = g\left(x, y\frac{Z_o}{Z}\right),$$

resulting in,

$$f(x, y, z) = \left(\frac{Z}{Zo}\right)^n g\left(x, y\frac{Zo}{Z}\right),$$

which is our stated theorem.

APPLICATIONS TO EXTENSIVE QUANTITIES

This theorem can be used in a variety of situations, we will consider some examples of its application. We will first consider the case when the degree of homogeneity is one.

First a trivial example. Given that the internal energy of a system for 3 moles of a substance is $E = pV^2$, what is the internal energy for N moles? We proceed as follows, we want E(p,V,N). The form of the theorem in this case is:

$$E(p, V, N) = \left(\frac{N}{N_o}\right) g\left(p, V\frac{N_o}{N}\right),$$

where $g(p,v) = pV^2$, and $N_o = 3$.
So,

$$E(P, V, N) = \frac{N}{3}\left\{P\left(\frac{V3}{N}\right)^2\right\} = 3\frac{pV^2}{N}.$$

As a second example, consider that the entropy of one mole of some substance is given by

$$s = R \ln (E^{3/2}V) + C.$$

Where C is a constant. What is the entropy for N moles of this material. Care must be exercised in this case because S is homogeneous of degree one in both E and V. This time we can write

$$S = \frac{N}{N_o}\left\{R \ln\left[\left(\frac{E N_o}{N}\right)^{3/2} \frac{V N_o}{N}\right] + C\right\},$$

but $N_o = 1$ so we get the result

$$S = N R \ln (E^{3/2} V N^{-5/2}) + NC.$$

APPLICATIONS TO INTENSIVE QUANTITIES

To apply the theorem to intensive quantities we set n, the degree of homogeneity, equal to zero in the theorem.

Again we will let the number of moles N play the role of the coordinate z so that $Z_o = N_o$.

Given the van der Waals equation of state for a single mole of gas,

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

where *R* is the ideal gas constant and *a* and *b* are constants. What is the van deer Waals equation of state for N moles? In this case the theorem becomes:

$$p(T, V, N) = p\left(T, V\frac{N_o}{N}\right),$$

so the pressure for N moles is:

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

This is of course the van der Waals equation for N moles.

DISCUSSION AND CONCLUSIONS

This paper has demonstrated the usefulness of homogeneous functions in thermodynamics. I have used the theorems presented in this paper in my thermal physics course for several years. I have found that a study of these theorems circumvents the usual tendency of students to scale thermodynamic results incorrectly. The theorems presented herein 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 the methods are not well known, they have been applied to other sub-fields of physics. Some examples are the applications to relativity by Lunn (1919), to communication theory by Shannon (1948a and 1948b), and to information theory by Haynes (1957). These applications, in addition to the applications mentioned previously, suggest that physicists should become more familiar with the techniques of application of functional equations. The theorem derived in this paper is useful for calculating general results from measurements made on fixed amounts of materials. The methods developed in this paper allow the student to develop an understanding of the mathematical techniques used in the application of homogeneous functions; this allows these students to concentrate on the physics of critical point phenomena when they are first met, thus affording a deeper understanding.

ACKNOWLEDGMENTS

This paper was written to honor the teaching career of Dr. Robert E. Kelly, formerly of the University of Mississippi, and currently at Los Alamos Scientific Laboratories. It was in his classroom that I learned the axiomatic approach to thermodynamics and much else. The basic methods of this paper were taught by Dr. Kelly for many years, though the particular forms and proofs presented above are due to the present author.

LITERATURE CITED

ACZEL, J. 1966. Lectures on Functional Equations and their applications. Academic Press. New York. 498 pp.

ACZEL, J. 1969. On Applications and theory of functional equations. Academic Press. New York. 63 pp.

CALLEN, H.B. 1960. Thermodynamics. Wiley. New York. 376 pp.

CHANDLER, DAVID. 1987. Introduction to modern statistical mechanics. Oxford University Press. New York. 274 pp.

DAVIS, HAROLD T. 1960. Introduction to non linear differential and integral equations. Atomic Energy Commission, Washington, D.C., 566 pp. (Reprinted by Dover. New York. 1962.)

EULER, L. 1755. Institutions Calculi Differentialis. Berlin. (Reprinted, Opera Omnia, Ser. I, Vol. 10. Leipzig. 1913.)

EULER, L. 1768. Institutiones, Calculi Integralis. Petropol. (Reprinted, Opera omnia, Ser. I, Vol. 11, Leipzig. 1913.)

EULER, L. 1770. Institutiones Calculi Integralis III. Petropol. (Reprinted, Opera Omnia, Ser. I, Vol. 13, Berlin. 1925.)

JAYNES, E.T. 1957. Information theory and statistical mechanics, I. Phys. Rev. 106:620-630.

LUNN, A.C. 1919. Some functional equations in the theory of relativity. Bull. Am. Math. Soc. 21:26-34.

SHANNON, C.E. 1948a. A mathematical theory of communication, I. Bell System Tech. J. 27:379-423.

SHANNON, C.E. 1948b. A mathematical theory of communication, II. Bell System Tech. J. 27:623-656.

STANLEY, H.E. 1971. Introduction to phase transitions and critical phenomena. Oxford University Press. New York. 308 pp.

TIEN, C.L. and J.H. LIENHARD. 1985. Statistical thermodynamics, Revised Printing. Hemisphere Publishing Corporation. New York. 397 pp.

WIDDER, D.V. 1961. Advanced calculus, 2nd E. Prentice-Hall. Englewood Cliffs. 520.pp.

ZEMANSKY, M.W. and R.H. DITTMAN. 1981. Heat and Thermodynamics, 6th Ed. McGraw-Hill. New York. 543 pp.

STEPHEN R. ADDISON, Department of Physics, University of Central Arkansas, Conway, AR 72032.

A SYNOPSIS OF THE NOTONECTIDAE OF ARKANSAS

There have been no studies pertaining specifically to the Notonectidae (back swimmers) of Arkansas. Pertinent information is either in taxonomic studies which include Arkansas material (Hungerford, 1933; Truxal, 1953) or aquatic macroinvertebrate lists from particular sites in the state (Harp and Hubbard, 1972; Harp and Harp, 1980; Farris and Harp, 1982; Huggins and Harp, 1983). The purposes of this paper are to present the first statewide species list, to delineate geographic distributions and to define preferred habitats for notonectid species in this state. Arkansas species may be identified by using Froeschner's (1962) key to Missouri species.

Most data presented have been synthesized from specimens in the Aquatic Macroinvertebrate Collection of the Arkansas State University Museum of Zoology; however contributions from museum collections from the Universities of Arkansas-Fayetteville and -Little Rock, along with literature records, are included. Supplemental collections were made by the authors to diminish distributional gaps in the data.

Two genera encompass the eight species of Notonectidae that occur in Arkansas. All species undergo five nymphal instars to reach adulthood and pass the winter as adults. Species of the two genera differ with respect to respiration, however. *Notonecta* species must surface frequently to replenish their oxygen supply. *Buenoa* individuals, however, have hemoglobin-filled abdominal sacs which greatly increase their capacity to store atmospheric oxygen (Truxal, 1953). This difference allows *Buenoa* to inhabit deeper water farther from shore and probably explains in part why fewer specimens of this genus are collected.

Buenoa confusa (Truxal) was first reported from Arkansas by Harp and Hubbard (1972). Distributionally, it is our least common notonectid, being represented by 35 specimens from 11 collections in three counties (Fig. 1). The collection in Monroe Co. contained three specimens taken by a black light trap. All other specimens were taken from the remaining two counties and were collected with a dipnet. Wilson (1958) reported this species in Mississippi from a single brackish pool filled with vegetation. In Arkansas, all collections were taken from clear, acid bauxite lakes, clear lakes or ponds with vegetation present. Arkansas collections thus far are from three ecoregions: Crowley's Ridge, the Ouachitas and the Mississippi Alluvial Plain. Truxal (1953) reported this species has been collected every month except February, March, October and December. Arkansas specimens have been collected during May and July-October.