

Dependent functions and constrained extrema – a mathematical analysis of thermodynamics:

Hans Huemer

Institute of Chemical Engineering Fundamentals and Plant Design
Graz University of Technology, Inffeldgasse 25, A-8010 Graz, Austria

Abstract

Thermodynamics was developed in the 19th century starting with a thorough analysis of processes and the behaviour of material systems. Gibbs condensed the knowledge of his time in postulative form and constructed a mathematical building, unsurpassed until today. Nevertheless many conceptions like e.g. entropy are not yet strictly defined, and some aspects of thermodynamics are difficult to understand. As example may serve, that the entropy of an adiabatically closed system should be a maximum although we know, that by definition of energy, volume and amount of the masses of the components any system is fully defined from mechanical point of view.

In this contribution the connections between functional dependence and constrained extremalization are examined. The mathematical analyse clarifies, why a quantity can be dependent on one hand, and at the same time be a constrained extremum on the other hand. The application of this perception on thermodynamics illuminates the essence of the Gibbs fundamental equation, expressing the functional dependence of the macroscopic entropy from energy, volume and mass, while at the same time entropy must be a maximum with respect to internal variables. Concerning the internal equilibria this shows the generality of the extremum principle, which seems not yet fully evaluated concerning equilibria between different forms of energy.

1. Introduction

Thermodynamics is difficult to understand, its correctness proved, its application most helpful in many branches of science and technology. The problem to understand it is documented by the fact, that even nowadays books are written about its fundamentals [1] and that its basis, the second law, called in german “principal sentence”, is far away from being expressed by one sentence.

The development of thermodynamics started empirical with some errors as described by Truesdell [2], but got a genius mathematical frame by Gibbs [7] at least for thermostatics. Gibbs had to choose a postulative approach according to the general state of science in his time, but several insights changed in the past 130 years.

It is the scope of this contribution to clarify some interdependencies between dependence of functions and constrained extremalization, both being important for the second law of thermodynamics. Applying the new mathematical viewpoints is not only helpful for better understanding of thermodynamics, but also shows the general principle behind the second law and thereby offers new possibilities for improvement of thermodynamic modelling in classical and statistical thermodynamics, some of them to be shown in succeeding publications.

2. Functional dependence and equivalence of constrained extremalization

In this part of the contribution the equivalence of functional dependence and the result of the derivation of the necessary conditions for constrained extrema by the procedure of Lagrange are to be shown. Then the new general aspects of this equivalence for functional systems are to be discussed.

2.1. Dependence of steady differentiable functions

First the necessary conditions for functional dependence are derived [4].

Given a system of m functions in n variables

$$\begin{aligned} f_1(x_1, \dots, x_n) &= 0 \\ f_2(x_1, \dots, x_n) &= 0 \\ &\dots\dots\dots \\ f_m(x_1, \dots, x_n) &= 0 \end{aligned} \tag{1}$$

with functional values u_1, u_2, \dots, u_m , then these functions are dependent, if a function

$$F(f_1(x_1, \dots, x_n), f_2(x_1, \dots, x_n), \dots, f_m(x_1, \dots, x_n)) = 0 \tag{2}$$

exists. Condition (2) is equivalent to the existence of a function

$$F(u_1, u_2, \dots, u_m) = 0 \tag{3}$$

u_i being the functional values of the functions f_1, \dots, f_m

In the case of dependence of the m functions the partial derivatives of F must be zero. This results in the following system of equation:

$$\begin{aligned} \left(\frac{\partial F}{\partial f_1}\right) \left(\frac{\partial f_1}{\partial x_1}\right) + \left(\frac{\partial F}{\partial f_2}\right) \left(\frac{\partial f_2}{\partial x_1}\right) + \dots + \left(\frac{\partial F}{\partial f_m}\right) \left(\frac{\partial f_m}{\partial x_1}\right) &= 0 \\ &\dots\dots\dots \\ \left(\frac{\partial F}{\partial f_1}\right) \left(\frac{\partial f_1}{\partial x_n}\right) + \left(\frac{\partial F}{\partial f_2}\right) \left(\frac{\partial f_2}{\partial x_n}\right) + \dots + \left(\frac{\partial F}{\partial f_m}\right) \left(\frac{\partial f_m}{\partial x_n}\right) &= 0 \end{aligned} \tag{4}$$

The vector

$$\left(\frac{\partial F}{\partial f_i}\right) = \left(\frac{\partial F}{\partial u_i}\right) \quad (i = 1, 2, \dots, m) \tag{5}$$

must be a non-zero vector due to the existence of equation (3) and therefore the system of equations (4) can be regarded as a homogeneous linear system of equations for the partial derivatives

$$\left(\frac{\partial f_i}{\partial x_j} \right) \quad (i = 1, 2, \dots, m; j = 1, 2, \dots, n) \tag{6}$$

This system has a non-zero solution only, if the rank of its Jacobian $r < m$, this being the usually evaluated condition of dependence. So it is possible, to check the necessary condition of functional dependence of the system of functions (1) by only proving the rank of its Jacobian without knowledge of the dependence function (2) resp. (3). The condition (4) therefore is usually of minor interest.

For later purposes of comparison with the necessary conditions for constrained extrema the system of equations (4) is of high interest here. First it can be stated, that the partial derivatives of the function of dependence (3) are independent of the variables x_i . The system

(4) can be divided by $\left(\frac{\partial F}{\partial f_1} \right)$ being non-zero as mentioned above.

Taking into account, that

$$\left(\frac{\partial F}{\partial f_i} \right) / \left(\frac{\partial F}{\partial f_1} \right) = - \left(\frac{\partial f_1}{\partial f_i} \right) \equiv -\lambda_i \tag{7}$$

the following system of equations results:

$$\left(\frac{\partial f_1}{\partial x_1} \right) - \lambda_2 \left(\frac{\partial f_2}{\partial x_1} \right) - \dots - \lambda_m \left(\frac{\partial f_m}{\partial x_1} \right) = 0$$

..... (8)

$$\left(\frac{\partial f_1}{\partial x_n} \right) - \lambda_2 \left(\frac{\partial f_2}{\partial x_n} \right) - \dots - \lambda_m \left(\frac{\partial f_m}{\partial x_n} \right) = 0$$

2.2. Lagrange’s method of undetermined multipliers

The system of functions (1) is examined again, but this time the task is, to calculate a vector $x_i (i = 1, \dots, n)$, for which the function value of $f_1(x_1, \dots, x_n)$ is an extremum (maximum or minimum) and which satisfies the functions f_2, \dots, f_m . There are several methods to solve this constrained extremalization problem described in literature [5].

The method of Lagrange’s undetermined multipliers is the oldest and mainly used in thermodynamics in connection with the extremum principle to derive the necessary conditions for constrained extrema. Most textbooks of mathematics describe the receipt without further explanation.

Instead of extremalizing the function $f_1(x_1, \dots, x_n)$ and taking into account the constraints by elimination of $(m-1)$ variables, which might be numerically impossible in practice, a function H is extremalized without constraints, where H is:

$$H(x_1, \dots, x_n) = f_1(x_1, \dots, x_n) - \lambda_2 f_2(x_1, \dots, x_n) - \dots - \lambda_m f_m(x_1, \dots, x_n) \tag{9}$$

$\lambda_2, \lambda_3, \dots, \lambda_m$ are arbitrary real numbers and not functions of the variables x_i , and x_i are regarded as independent variables. Necessary conditions for an extremum of H are therefore:

$$\left(\frac{\partial H}{\partial x_1}\right) = 0; \left(\frac{\partial H}{\partial x_2}\right) = 0; \dots; \left(\frac{\partial H}{\partial x_n}\right) = 0 \tag{10}$$

Solution of the system of equations (10) together with the given constraints $f_2(x_1, \dots, x_n), \dots, f_m(x_1, \dots, x_n)$ gives the vectors (x_1, \dots, x_n) and $(\lambda_2, \dots, \lambda_m)$ for which f_1 is a constrained extremum. The Lagrangian multipliers $\lambda_2, \dots, \lambda_m$ are the differentials of the objective functions in the constraints. They are named sensitivity coefficients [5].

$$\lambda_1 = \left(\frac{\partial f_1}{\partial f_2}\right), \dots, \lambda_m = \left(\frac{\partial f_1}{\partial f_m}\right) \tag{11}$$

They give the change of the objective functions with a change in the given constraints. Performing the derivations of the necessary conditions for an extremum of H (eq. (10) in detail results in:

$$\begin{aligned} \left(\frac{\partial f_1}{\partial x_1}\right) - \lambda_2 \left(\frac{\partial f_2}{\partial x_1}\right) - \dots - \lambda_m \left(\frac{\partial f_m}{\partial x_1}\right) &= 0 \\ \dots \dots \dots \tag{12} \\ \left(\frac{\partial f_1}{\partial x_n}\right) - \lambda_2 \left(\frac{\partial f_2}{\partial x_n}\right) - \dots - \lambda_m \left(\frac{\partial f_m}{\partial x_n}\right) &= 0 \end{aligned}$$

A comparison of equation (12) with equation (8) shows them to be identical. This is first showing the mathematical background of the Lagrangian procedure – a functional dependence of the objective function from the constraint functions is a necessary condition for a constrained extremum, this certainly only true for tight constraints. It is remarkable, that no textbook of mathematics or optimization, not even the excellent book of Wilde and Beightler, either derives the Lagrangian procedure or mentions this identity. This might be due to the fact, that it is trivial for a mathematician, but it is nevertheless most important for thermodynamics, where the extremum principle is nearly regarded as postulate.

2.3. Summarizing mathematical considerations

The identity of the results shows the equivalence of both methods. The usual aim of checking the rank of the Jacobian matrix is to find out functional dependence. For this the system of equations (8) is of no interest.

The Lagrangian method was the first to solve constrained extremum problems. While for the check of functional dependence the form of the correlation between the functional values is of no interest, this interrelation is a by-product of the Lagrange-procedure, since equation (9) can be formulated knowing the Lagrangian multipliers.

So it is possible to derive a function for the functional values of a system of dependent functions using the Lagrangian procedure of constrained optimization. This function is exactly the Lagrangian equation (9) for H. This is the main result of the mathematical part of the contribution.

Before applying this result to thermodynamics, let us summarize:

Let us assume, a general function

$$F(u_1, u_2, \dots, u_m) = 0 \tag{13}$$

in macroscopic variables u_i exists although we might not know it, then at least theoretically each variable (e.g. u_1) can be isolated and expressed as function of the other (independent) variables.

$$u_1 = f(u_2, u_3, \dots, u_m) \tag{14}$$

Its total differential is given by:

$$du_1 = \left(\frac{\partial u_1}{\partial u_2}\right) du_2 + \left(\frac{\partial u_1}{\partial u_3}\right) du_3 + \dots + \left(\frac{\partial u_1}{\partial u_m}\right) du_m \tag{15}$$

If the variables u_1, \dots, u_m are functional values of a vector of (internal) variables (x_1, x_2, \dots, x_n) , an additional functional system exists:

$$\begin{aligned} u_1 &= \varphi_1(x_1, \dots, x_n) \\ u_2 &= \varphi_2(x_1, \dots, x_n) \\ &\dots\dots\dots \\ u_m &= \varphi_m(x_1, \dots, x_n) \end{aligned} \tag{16}$$

This system is equivalent to the functional system equation (1), giving the functional values explicitly.

If equation (13) resp. (14) exists, these functions must simultaneously be dependent on one hand and each of the variables u_1, \dots, u_m must be a constrained extremum with respect to the variables x_i , the other variables u_i being constant constraints, on the other hand. The choice of the objective function is arbitrary.

For u_1 being the objective function equation (15) is not only the total differential of (14), but at the same time the sensitivity equation.

The differentials

$$\left(\frac{\partial u_1}{\partial u_i}\right) = \lambda_i \neq \lambda(x_i) \tag{17}$$

are the Lagrangian multipliers or sensitivity coefficients, depending on the values u_2, \dots, u_m , but not on the internal variables x_i . This is of importance concerning performance of Legendre transformations, that means substitution of one or more of the constraints (u_2, \dots, u_m) by the derivatives λ_i . Since the λ_i are not functions of the x_i , one constraint (or more) would be lost, if the internal variables are not transformed too.

Most important for thermodynamic and any other kind of modelling is the following consequence of the equivalence:

Knowing, that different quantities like u_1, u_2, \dots, u_m are important for the state or behaviour of a system and furthermore knowing the functional dependencies of these u_i from a set of variables x_i (system of equations (16)), but not knowing the interrelation of these u_i , the Lagrangian procedure permits to derive this macroscopic functional interrelation between the macroscopic variables u_i in integral form (eq. (9)) and differential form (equation (15)). So the

Lagrangian procedure is not only valuable for constrained extremalization problems, but also for the evaluation of functional systems.

The best example for this is thermodynamics. We know that macroscopically the energy, the volume and the masses of the particles must be sufficient to characterize any mechanical system. Knowing furthermore, that an additional macroscopic quantity exists (e.g. entropy) and knowing functional dependencies of these macroscopic quantities from a set of internal variables, we can derive a correlation between the macroscopic quantities by the Lagrangian procedure, this being the integral form of the Gibbs fundamental equation.

3. General formulation of the thermodynamic extremum principle

In this part the mathematical considerations of chapter 2 are applied to thermodynamics. Starting point is the axiomatic formulation of the II law of thermodynamics given by Gibbs. The application of mathematics clarifies not only the postulates of Gibbs, but also shows further possibilities of thermodynamic modelling.

3.1. General axiomatic formulation of the II law of thermodynamics by Gibbs

It was the merit of J.W. Gibbs [7] to formulate thermodynamics in a universal manner including all possible phenomena being of interest for thermodynamic systems. Here a restriction to phenomena important for phase equilibria and phase properties is made, therefore excluding electrochemical, surface phenomena etc.

According to Münster [3] the following basic statements are formulated as postulates by Gibbs for systems in equilibrium:

a. For every phase α a state-function S named entropy exists:

$$S^{(\alpha)} = S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, \dots, N_m^{(\alpha)}) \quad (18)$$

b. The differential of entropy is given by:

$$T^{(\alpha)} dS^{(\alpha)} = dU^{(\alpha)} + P^{(\alpha)} dV^{(\alpha)} - \sum_{i=1}^m \mu_i^{(\alpha)} dN_i^{(\alpha)} \quad (19)$$

c. The entropy of the total system is:

$$S = \sum_{\alpha} S^{(\alpha)} \quad (20)$$

d. For adiabatically closed systems is valid:

$$dS \geq 0 \quad (21)$$

Equations (1) and (2) are called Gibbs fundamental equations in integral and differential form. This basis permits the derivation of all thermodynamic state variables and relations by formal

mathematic operations. So the postulates (18) – (21) are the most concise and comprehensive formulation of the II law of thermodynamics.

3.2. Mathematic and physical discussion

When Gibbs published his fundamental work from 1873 to 1878 the sight of science was different from today and many facts accepted now were in discussion, e.g. the atomistic theory. This certainly caused some cautious formulations.

First we may stress, that entropy as an extensive property for phases in equilibrium must be an extensive variable of state anyway (20). Equation (21) tells, that the entropy of the system must be a maximum, this meaning that for adiabatically closed systems entropy is a dependent function. Gibbs [7] furthermore accented, that a maximum of entropy at constant energy is equivalent to a minimum of energy at constant entropy. This is a further hint, that already Gibbs assumed functional dependence.

For this functional dependence it is necessary, that the fundamental equations:

$$S = S(U, V, N_1, \dots, N_m) \quad (22)$$

and

$$T dS = dU + P dV - \sum_{i=1}^m \mu_i dN_i \quad (23)$$

are also valid for the adiabatically closed system as whole.

The 4 postulates of Gibbs therefore may be reduced to 2 under the light of equivalence of functional dependence and extremalization. Equations (22) and (23) resp. (18) and (19) without phase index are universally valid for every system, homogeneous or heterogeneous. Equation (23) being the total differential of (22) is the most concise definition of the intensive state variables T, P and μ_i . The distinction between different problems like phase-equilibria, reaction equilibria or statistical mechanical problems lies in the different sets of internal variables the macroscopic or system variables (S, U, V, N) are dependent of.

For a multiphase system S, U, V, N_i of the phases are the internal variables of the total system, for each phase again (22) and (23) being valid. Solution of this extremalization leads to the condition of phase equilibria ([7],[3]), that means equality of temperature, pressure and chemical potentials of the components in the phases.

For chemical reacting systems the mole numbers of the different species are to be taken as internal variables, this leading to the usual reaction-equilibrium conditions.

The most interesting case is doubtless the homogeneous system. Internal variables are here the different forms of energies (kinetic, potential, oscillatory etc.), since the energy U must be the total energy, that means the sum of these forms. Furthermore each of these forms of energy must also show a distribution over different energy states, the system value of the energy form then being the sum of the energy states. For systems with only kinetic energy the application of the extremum principle must lead to a Boltzmann distribution. Equilibria between the different forms of energy can only be calculated, if we can attribute to each form of energy an according dependence of entropy. This necessitates functional dependencies also for the entropy and therefore its clear definition. A possibility for this will be shown in a following paper. It should be anticipated, that this and the application of the extremum principle offer a new way of thermodynamic modelling, whereby conventional equations of

state can be derived (like the cubic type), but also improved ones, where equilibria between kinetic, potential and other forms of energy may be taken into account.

4. Conclusions

The mathematical considerations, stemming from the equivalence of the necessary criteria of functional dependence and constrained extremalization, show, that the postulates of Gibbs can be reduced to the general statement of his fundamental equation in integral and differential form. These can be applied to any type of equilibrium problem (phase, reaction and internal equilibria between the different forms of energy).

The usual derivation of the second law of thermodynamics (e.g. [6] or [8]) stems from an analysis of the Carnot cycle. This is not quite satisfying from physical point of view, since all processes are only examples of a general principle and not the principle itself.

The Gibbs fundamental equation and its generality needs not to be postulated, but can be argued in a different manner.

Following the principles of mechanics (e.g. [9]) we can state, that any mechanical system is fully defined by its energy, its mass and its extension in space. For adiabatically closed multibody systems this is the internal energy U , the masses or moles of the components N_i and the volume V . Any other variable or property of the system must be defined and consequently be dependent. It is this dependence, which is expressed by the Gibbs fundamental equation.

These facts and the mathematic of functional dependency and extremalization are the frame for further developments in thermodynamic modelling, as to be shown in succeeding papers.

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