Relationships between partial derivatives of Legendre transforms - applications in thermodynamics

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ABSTRACT. Legendre transforms and their applications in thermodynamics are revisited by the use of Jacobian representation in order to express second order partial derivatives of a Legendre transform in terms of another Legendre transform. Some examples are shown to demonstrate the simplicity and conciseness power of the method.

Key words: Legendre transforms, jacobian formulation, thermodynamic relationships.

RESUMO. O relacionamento entre os derivados parciais das transformadas de Legendre e suas aplicações termodinâmicas. Transformadas de Legendre e suas aplicações em termodinâmica são revisitadas, através do uso da representação jacobiana para relacionar derivadas parciais de segunda ordem de uma transformada de Legendre de determinada ordem às de uma transformada de Legendre de outra ordem qualquer. Exemplos são apresentados para demonstrar a simplicidade e poder de síntese do método.

Palavras-chave: transformadas de Legendre, formulação jacobiana, relações termodinâmicas.

In classical thermodynamics, there are several equivalent forms of the fundamental equation, whose knowledge means the access to all conceivable thermodynamic information about the system. The art of solving problems in thermodynamics lies largely in the selection of the most convenient form for each particular case. A classical example is the thermodynamic stability analysis of simple systems where this selection is fundamental for conciseness and clarity of the implied criteria representation (Tester and Modell, 1997).

In this context, the theory of Legendre transforms play a preponderant role and its application in thermodynamics has been frequently illustrated (Tisza, 1966); Beegle *et al*. (1974), Modell and Reid (1982), Kumar and Reid (1986), Tester and Modell (1997). Kumar and Reid (1986), using Jacobian formulation, present a simple and concise method to obtain expressions for partial derivatives of Legendre transforms in terms of a base function and also indicate the possibility of extending the method.

Despite being a well known technique, the use of Jacobian formulation in thermodynamics has been frequently disregarded in favor of less simple and concise methods. At other times, its use in very specific cases, does not stimulate its application in broader situations.

In this paper, Jacobian formulation is used in order to obtain general relationships between partial derivatives of Legendre transforms of different orders. The use of this technique is shown through examples, some of them presenting the development of well known relations in thermodynamics.

Method development

The k-th Legendre transform of the base function $y^{(0)}(x_1, x_2, \ldots, x_n)$ may be represented by

$$y^{(k)} = y^{(0)} - \sum_{i=1}^{k} \xi_i x_i \tag{1}$$

where,

$$\xi_i = \left.\frac{\partial y^{(0)}}{\partial x_i}\right|_{x_1, x_2, \ldots, x_{i-1}, x_{i+1}, \ldots, x_n} \equiv y_i^{(0)} \tag{2}$$

The following differential form is obtained from (1):

$$dy^{(k)} = \sum_{i=1}^{k} (-x_i) d\xi_i + \sum_{i=k+1}^{n} \xi_i dx_i \tag{3}$$

Thus $y^{(k)}$ is a function of the conjugated and original variables $\xi_1, ..., \xi_k, x_{k+1}, ..., x_n$ and it is observed that only the first k variables are different from the correspondent ones in $y^{(0)}(x_1, x_2, ..., x_k, x_{k+1}, ..., x_n)$. Thus, given the order (k) of a Legendre transform, the independent variables of $y^{(k)}$ are completely specified for each ordering of the $y^{(0)}$ variables.

The first order derivatives of $y^{(k)}$ may be represented by:

$$y_i^{(k)} \equiv \begin{cases} \left.\dfrac{\partial y^{(k)}}{\partial \xi_i}\right|_{\xi_1,\dots,\xi_{i-1},\xi_{i+1},\dots,\xi_k,x_{k+1},\dots,x_n} = -x_i & (i \le k) \\ \left.\dfrac{\partial y^{(k)}}{\partial x_i}\right|_{\xi_1,\dots,\xi_k,x_{k+1},\dots,x_{i-1},x_{i+1},\dots,x_n} = \xi_i & (i > k) \end{cases} \quad (4)$$

where the notation for derivatives indicates, in addition, all variables kept constant during the operation. An alternative representation of (4) is given by

$$\begin{aligned} y_i^{(i)} &= y_i^{(i+1)} = \dots = y_i^{(n)} = -x_i \\ y_i^{(i-1)} &= y_i^{(i-2)} = \dots = y_i^{(0)} = \xi_i \end{aligned} \quad (4\text{-a})$$

Consequently, the second order partial derivatives of $y^{(k)}$ may be represented by

$$y_{ij}^{(k)} \equiv \begin{cases} \left.\dfrac{\partial \xi_i}{\partial x_j}\right|_{\xi_1,\dots,\xi_k,x_{k+1},\dots,x_{j-1},x_{j+1},\dots,x_n} & (i, j > k) \\ \left.\dfrac{\partial(-x_i)}{\partial x_j}\right|_{\xi_1,\dots,\xi_k,x_{k+1},\dots,x_{j-1},x_{j+1},\dots,x_n} & (i \le k \text{ e } j > k) \\ \left.\dfrac{\partial(-x_i)}{\partial \xi_j}\right|_{\xi_1,\dots,\xi_{j-1},\xi_{j+1},\dots,\xi_k,x_{k+1},\dots,x_n} & (i, j \le k) \end{cases} \quad (5)$$

The Jacobian of a set of functions $(\alpha_1, \alpha_2, ..., \alpha_n)$, with independent variables $(\beta_1, \beta_2, ..., \beta_n)$, is represented by

$$\frac{\partial(\alpha_1,\alpha_2,\dots,\alpha_n)}{\partial(\beta_1,\beta_2,\dots,\beta_n)} = \begin{vmatrix} \dfrac{\partial\alpha_1}{\partial\beta_1} & \dfrac{\partial\alpha_1}{\partial\beta_2} & \cdots & \dfrac{\partial\alpha_1}{\partial\beta_n} \\ \dfrac{\partial\alpha_2}{\partial\beta_1} & \dfrac{\partial\alpha_2}{\partial\beta_2} & \cdots & \dfrac{\partial\alpha_2}{\partial\beta_n} \\ \vdots & \vdots & \cdots & \vdots \\ \dfrac{\partial\alpha_n}{\partial\beta_1} & \dfrac{\partial\alpha_n}{\partial\beta_2} & \cdots & \dfrac{\partial\alpha_n}{\partial\beta_n} \end{vmatrix} \quad (6)$$

where $\dfrac{\partial\alpha_i}{\partial\beta_j}$ stands for $\left.\dfrac{\partial\alpha_i}{\partial\beta_j}\right|_{\beta_1,\beta_2,\dots,\beta_{j-1},\beta_{j+1},\dots,\beta_n}$.

Invoking Jacobian properties it is possible to rewrite equation (5) in the following generic form:

$$y_{ij}^{(k)} = \left.\frac{\partial\alpha_i}{\partial\beta_j}\right|_{\beta_1,\beta_2,\dots,\beta_{j-1},\beta_{j+1},\dots,\beta_n} = \frac{\partial(\beta_1,\beta_2,\dots,\beta_{j-1},\alpha_i,\beta_{j+1},\dots,\beta_n)}{\partial(\beta_1,\beta_2,\dots,\beta_{j-1},\beta_j,\beta_{j+1},\dots,\beta_n)} \quad (7)$$

where $(\beta_1, \beta_2, ..., \beta_n) = (\xi_1, ..., \xi_k, x_{k+1}, ..., x_n)$ are the independent variables of $y^{(k)}$.

Using the chain rule for derivatives, it is possible to relate $y_{ij}^{(k)}$ to derivatives of $y^{(s)}$ $(s \neq k)$, in the following way

$$y_{ij}^{(k)} = \frac{\partial(\beta_1,\beta_2,\dots,\beta_{j-1},\alpha_i,\beta_{j+1},\dots,\beta_n)}{\partial(\xi_1,\dots,\xi_s,x_{s+1},\dots,x_n)} \div \frac{\partial(\beta_1,\beta_2,\dots,\beta_{j-1},\beta_j,\beta_{j+1},\dots,\beta_n)}{\partial(\xi_1,\dots,\xi_s,x_{s+1},\dots,x_n)} \quad (8)$$

Equation (8) is the base for relating second order partial derivatives of a Legendre transform to the derivatives of another Legendre transform. This equation may have alternative representations depending on the use of Jacobian properties related to elimination, ordering and signal change of the involved variables. The examples presented in this paper show these aspects and also indicate possible shortcuts for the method. Such alternative representations and shortcuts are based on the following Jacobian properties:

(i)-elimination of variables

$$\frac{\partial(\alpha_1,\dots,\alpha_{j-1},\alpha_j,\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,\beta_{j-1},\alpha_j,\beta_{j+1},\dots,\beta_n)} = \frac{\partial(\alpha_1,\dots,\alpha_{j-1},\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,\beta_{j-1},\beta_{j+1},\dots,\beta_n)} \quad (9)$$

(ii)-ordering of variables

$$\frac{\partial(\alpha_1,\dots,\alpha_{i-1},\alpha_i,\alpha_{i+1},\dots,\alpha_j,\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,\beta_n)} = (-1)^{j-i}\,\frac{\partial(\alpha_1,\dots,\alpha_{i-1},\alpha_{i+1},\dots,\alpha_j,\alpha_i,\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,\beta_n)} \quad (10)$$

(iii)- signal change of variables

$$\frac{\partial(\alpha_1,\dots,-\alpha_j,\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,\beta_j,\beta_{j+1},\dots,\beta_n)} = \frac{\partial(\alpha_1,\dots,\alpha_j,\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,-\beta_j,\beta_{j+1},\dots,\beta_n)} = -\frac{\partial(\alpha_1,\dots,\alpha_j,\alpha_{j+1},\dots,\alpha_n)}{\partial(\beta_1,\dots,\beta_j,\beta_{j+1},\dots,\beta_n)} \quad (11)$$

Examples

Example 1: Develop an expression that relates $y_{23}^{(4)}$ to the derivatives of $y^{(1)}$.

The observed derivative may be represented by equation (5), for the case $(i, j \le k)$. Thus,

$$y_{23}^{(4)} \stackrel{(5)}{=} \left.\frac{\partial(-x_2)}{\partial \xi_3}\right|_{\xi_1,\xi_2,\xi_4,x_5,\ldots,x_n} \stackrel{(8)}{=} \frac{\partial(\xi_1,\xi_2,-x_2,\xi_4,x_5,\ldots,x_n)}{\partial(\xi_1,x_2,x_3,x_4,x_5,\ldots,x_n)} \div \frac{\partial(\xi_1,\xi_2,\xi_3,\xi_4,x_5,\ldots,x_n)}{\partial(\xi_1,x_2,x_3,x_4,x_5,\ldots,x_n)} \stackrel{(11)}{=}$$

$$-\frac{\partial(\xi_1,\xi_2,x_2,\xi_4,x_5,\ldots,x_n)}{\partial(\xi_1,x_2,x_3,x_4,x_5,\ldots,x_n)} \div \frac{\partial(\xi_1,\xi_2,\xi_3,\xi_4,x_5,\ldots,x_n)}{\partial(\xi_1,x_2,x_3,x_4,x_5,\ldots,x_n)} \stackrel{(10)}{=}$$

$$\frac{\partial(\xi_1,x_2,\xi_2,\xi_4,x_5,\ldots,x_n)}{\partial(\xi_1,x_2,x_3,x_4,x_5,\ldots,x_n)} \div \frac{\partial(\xi_1,\xi_2,\xi_3,\xi_4,x_5,\ldots,x_n)}{\partial(\xi_1,x_2,x_3,x_4,x_5,\ldots,x_n)} \stackrel{(9)}{=} \frac{\partial(\xi_2,\xi_4)}{\partial(x_3,x_4)} \div \frac{\partial(\xi_2,\xi_3,\xi_4)}{\partial(x_2,x_3,x_4)}$$

Using equation (6), the result may be expressed as (Tester and Modell (1997), Example 5.7):

$$y_{23}^{(4)} = \begin{vmatrix} y_{23}^{(1)} & y_{24}^{(1)} \\ y_{34}^{(1)} & y_{44}^{(1)} \end{vmatrix} \div \begin{vmatrix} y_{22}^{(1)} & y_{23}^{(1)} & y_{24}^{(1)} \\ y_{23}^{(1)} & y_{33}^{(1)} & y_{34}^{(1)} \\ y_{24}^{(1)} & y_{34}^{(1)} & y_{44}^{(1)} \end{vmatrix} \qquad (12)$$

Example 2: Develop an expression that relates $U_{SN_1} = \dfrac{\partial^2 U(S,V,N_1,\ldots,N_n)}{\partial S \partial N_1}$ to the derivatives of $G(T,P,N_1,\ldots,N_n)$.

In this case, considering $x_1=S$, $x_2=V$ and $x_i=N_{i-2}$ for $i>2$, it follows that $\xi_1=T$, $\xi_2=-P$, $y^{(0)}=U$, $y^{(2)}=G$ e $U_{SN_1} = y_{13}^{(0)}$ and

$$y_{13}^{(0)} \stackrel{(5)}{=} \left.\frac{\partial \xi_1}{\partial x_3}\right|_{x_1,x_2,x_4,\ldots,x_n} \stackrel{(8)}{=} \frac{\partial(x_1,x_2,\xi_1,x_4,\ldots,x_n)}{\partial(\xi_1,\xi_2,x_3,x_4,\ldots,x_n)} \div \frac{\partial(x_1,x_2,x_3,x_4,\ldots,x_n)}{\partial(\xi_1,\xi_2,x_3,x_4,\ldots,x_n)} \stackrel{(9),(10)}{=}$$

$$\frac{\partial(x_1,x_2)}{\partial(\xi_2,x_3)} \div \frac{\partial(x_1,x_2)}{\partial(\xi_1,\xi_2)} \stackrel{(11)}{=} \frac{\partial(-x_1,-x_2)}{\partial(\xi_2,x_3)} \div \frac{\partial(-x_1,-x_2)}{\partial(\xi_1,\xi_2)} \stackrel{(6)}{=}$$

$$\begin{vmatrix} y_{12}^{(2)} & y_{13}^{(2)} \\ y_{22}^{(2)} & y_{23}^{(2)} \end{vmatrix} \div \begin{vmatrix} y_{11}^{(2)} & y_{12}^{(2)} \\ y_{12}^{(2)} & y_{22}^{(2)} \end{vmatrix} = \begin{vmatrix} G_{T(-P)} & G_{TN_1} \\ G_{(-P)(-P)} & G_{(-P)N_1} \end{vmatrix} \div \begin{vmatrix} G_{TT} & G_{T(-P)} \\ G_{T(-P)} & G_{(-P)(-P)} \end{vmatrix}$$

Finally:

$$U_{SN_1} = \begin{vmatrix} G_{TP} & G_{TN_1} \\ G_{PP} & G_{PN_1} \end{vmatrix} \div \begin{vmatrix} G_{TT} & G_{TP} \\ G_{TP} & G_{PP} \end{vmatrix} \qquad (13)$$

where,

$$G_{TT} = \frac{\partial^2 G(T,P,N_1,\ldots,N_n)}{\partial T^2} \quad , \quad G_{TP} = \frac{\partial^2 G(T,P,N_1,\ldots,N_n)}{\partial T \partial P}$$

and so on.

Example 3: Develop an expression that relates $y_{ij}^{(k)}$ to the derivatives of $y^{(k-1)}$, for $i,j>k$.

Considering that $j \geq i$ (second order derivatives in this paper do not depend on the order of derivation so that such hypothesis involves no loss of generality), it follows that

$$y_{ij}^{(k)} = \left.\frac{\partial \xi_i}{\partial x_j}\right|_{\xi_1,\ldots,\xi_k,x_{k+1},\ldots,x_{j-1},x_{j+1},\ldots,x_n} = \frac{\partial(\xi_1,\ldots,\xi_{k-1},\xi_k,x_{k+1},\ldots,x_{j-1},\xi_i,x_{j+1},\ldots,x_n)}{\partial(\xi_1,\ldots,\xi_{k-1},x_k,x_{k+1},\ldots,x_{j-1},x_j,x_{j+1},\ldots,x_n)} \div$$

$$\frac{\partial(\xi_1,\ldots,\xi_{k-1},\xi_k,x_{k+1},\ldots,x_{j-1},x_j,x_{j+1},\ldots,x_n)}{\partial(\xi_1,\ldots,\xi_{k-1},x_k,x_{k+1},\ldots,x_{j-1},x_j,x_{j+1},\ldots,x_n)} = \frac{\partial(\xi_k,\xi_i)}{\partial(x_k,x_i)} \div \frac{\partial(\xi_k)}{\partial(x_k)} = \begin{vmatrix} y_{kk}^{(k-1)} & y_{kj}^{(k-1)} \\ y_{ki}^{(k-1)} & y_{ij}^{(k-1)} \end{vmatrix} \div y_{kk}^{(k-1)}$$

therefore,

$$y_{ij}^{(k)} = y_{ij}^{(k-1)} - \frac{y_{ki}^{(k-1)} y_{kj}^{(k-1)}}{y_{ij}^{(k-1)}} \qquad (14)$$

Special cases:
(a) k=1 (Beegle *et al*. (1974), Table 1)

$$y_{ij}^{(1)} = y_{ij}^{(0)} - \frac{y_{1i}^{(0)} y_{1j}^{(0)}}{y_{ij}^{(0)}} \qquad (15)$$

(b) i=j=s e k=(s-1) (Tester and Modell (1997), eq. 7-14)

$$y_{ss}^{(s-1)} = y_{ss}^{(s-2)} - \frac{\left(y_{(s-1)s}^{(s-2)}\right)^2}{y_{ss}^{(s-2)}} \qquad (16)$$

Example 4: A relation used in thermodynamic stability analysis of simple systems is presented in Tester and Modell (1997) equation (7-20). For $y^{(0)} = y^{(0)}(x_1,\ldots,x_n)$ it may be represented by:

$$y_{(n-1)(n-1)}^{(n-2)} = \begin{cases} = L_i & i = (n-2) \\ = \dfrac{L_i}{\prod\limits_{r=i}^{(n-3)} y_{(r+1)(r+1)}^{(r)}} & i < (n-2) \end{cases} \qquad (17)$$

where,

$$L_i \equiv \frac{\partial(\xi_{i+1},\ldots,\xi_{n-1})}{\partial(x_{i+1},\ldots,x_{n-1})} \qquad (18)$$

Initiallly, it results immediately from (18) that for i = (n-2):

$$y_{(n-1)(n-1)}^{(n-2)} = \left.\frac{\partial \xi_{n-1}}{\partial x_{n-1}}\right|_{\xi_1,\ldots,\xi_{n-2},x_{n-2},\ldots,x_n} = L_{n-2}$$

On the other hand, it may be seen that for i < (n-2):

$$y^{(n-2)}_{(n-1)(n-1)} = \left.\frac{\partial \xi_{n-1}}{\partial x_{n-1}}\right|_{\xi_1,\dots,\xi_{n-2},x_n} \overset{(6)}{=}$$

$$\frac{\partial(\xi_1,\dots,\xi_i,\xi_{i+1},\dots,\xi_{n-2},\xi_{n-1},x_n)}{\partial(\xi_1,\dots,\xi_i,x_{i+1},\dots,x_{n-2},x_{n-1},x_n)} \div \frac{\partial(\xi_1,\dots,\xi_i,\xi_{i+1},\dots,\xi_{n-2},x_{n-1},x_n)}{\partial(\xi_1,\dots,\xi_i,x_{i+1},\dots,x_{n-2},x_{n-1},x_n)} \overset{(9)}{=}$$

$$\frac{\partial(\xi_{i+1},\dots,\xi_{n-2},\xi_{n-1})}{\partial(x_{i+1},\dots,x_{n-2},x_{n-1})} \div \frac{\partial(\xi_{i+1},\dots,\xi_{n-2})}{\partial(x_{i+1},\dots,x_{n-2})} \overset{(18)}{=} L_i \div \frac{\partial(\xi_{i+1},\dots,\xi_{n-2})}{\partial(x_{i+1},\dots,x_{n-2})}$$

Similarly, it follows that:

$$y^{(n-3)}_{(n-2)(n-2)} = \frac{\partial(\xi_{i+1},\dots,\xi_{n-2})}{\partial(x_{i+1},\dots,x_{n-2})} \div \frac{\partial(\xi_{i+1},\dots,\xi_{n-3})}{\partial(x_{i+1},\dots,x_{n-3})}$$

$$\vdots \qquad\qquad \vdots$$

$$y^{(i+1)}_{(i+2)(i+2)} = \frac{\partial(\xi_{i+1},\xi_{i+2})}{\partial(x_{i+1},\dots,x_{i+2})} \div \frac{\partial(\xi_{i+1})}{\partial(x_{i+1})}$$

$$y^{(i)}_{(i+2)(i+2)} = \frac{\partial(\xi_{i+1})}{\partial(x_{i+1})}$$

Multiplying all the above equations for $i < (n-2)$, it is found that:

$$y^{(n-2)}_{(n-1)(n-1)} \times \prod_{r=i}^{(n-3)} y^{(r)}_{(r+1)(r+1)} = L_i$$

The second part of equation (17) follows immediately from this last relation. The above demonstration represents a simpler and more concise alternative than that in Tester and Modell (1997), chapter 5, section 5-9.

A general method was presented, based on Jacobian formulation, relating second order partial derivatives of a Legendre transform in terms of another Legendre transform. The simplicity and conciseness power of this method were shown through examples, some of them involving well known relations in thermodynamics. The method can be extended to higher order derivatives.

The proposed method does not differ significantly from the works of Beegle *et al*. (1974) and of Tester and Modell (1997), but the procedure presented above may allow a better understanding of this powerful technique.

Symbology

G	- Gibbs free energy
N_i	- mols of component i
P	- pressure
S	- entropy
T	- temperature
U	- internal energy
V	- volume
x_i	- original variable of the base function
$y^{(0)}$	- base function
$y^{(k)}$	- k-th Legendre transform of $y^{(0)}$
$y_i^{(k)}, y_{ij}^{(k)}$	- first and second order derivatives of $y^{(k)}$
L_i	- determinant defined by equation (18)
ξ_i	- conjugated variable of x_i in Legendre transform representation
$\frac{\partial(\alpha_1,\alpha_2,\dots,\alpha_n)}{\partial(\beta_1,\beta_2,\dots,\beta_n)}$	- Jacobian of the set of functions: $\{\alpha_i(\beta_1,\dots,\beta_n);\ i=1,2,\dots,n\}$

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