Derivation of the Relationships between Partial Derivatives of Legendre Transforms

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Legendre transforms have a variety of applications in classical thermodynamics. The general theory of these transforms and their applicability to chemical thermodynamics has been illustrated by Tisza (1966), Beegle et al., (1974), and Modell and Reid (1982). Beegle et al. present expressions, without proof, for the second partial derivatives of any Legendre transform in terms of partial derivatives of the basis function, $y^{(0)}$. These expressions cannot be derived in any straightforward manner, as the bookkeeping involved becomes very cumbersome. In this note, we derive these formulae by using a mathematical technique (Tisza, 1966) that retains the required mathematical consistency while being deceptively simple. Also presented are techniques for expressing the partial derivatives of any transform in terms of the partial derivatives of any other transform. The method can be extended to higher order derivatives if desired.

Derivation

We wish to derive expressions for any second partial derivative of the kth Legendre transform, $y_{ij}^{(k)}$, in terms of the partial derivatives of the basis function, $y^{(0)}$. Three different cases can be envisaged, namely:

1. $i, j > k$
2. $i \le k, j > k$ (by symmetry, the case $i > k, j \le k$ is identical except for interchanging the indices i and j)
3. $i \le k, j \le k$

Case 1: i, j > k

Using standard notation we can represent the derivative $y_{ij}^{(k)}$ as,

$$y_{ij}^{(k)} = \left[\frac{\partial \xi_i}{\partial x_j}\right]_{\xi_1, \xi_2 \ldots \xi_k, x_{k+1} \ldots x_{j-1}, x_{j+1} \ldots x_N} \tag{1}$$

which can be rewritten in a Jacobian formulation as,

$$y_{ij}^{(k)} = \frac{\partial(\xi_1, \xi_2, \ldots \xi_k, \xi_i)}{\partial(\xi_1, \xi_2, \ldots \xi_k, x_j)} \tag{2}$$

or in matrix representation,

$$= \begin{vmatrix} \left.\dfrac{\partial \xi_1}{\partial \xi_1}\right|_{\xi_{[1]}, x_1} & \cdots & \left.\dfrac{\partial \xi_i}{\partial \xi_1}\right|_{\xi_{[1]}, x_1} \\ \left.\dfrac{\partial \xi_1}{\partial \xi_2}\right|_{\xi_{[2]}, x_1} & \cdots & \left.\dfrac{\partial \xi_i}{\partial \xi_2}\right|_{\xi_{[2]}, x_1} \\ \vdots & & \vdots \\ \left.\dfrac{\partial \xi_1}{\partial x_j}\right|_{\xi_1, x_{[j]}} & \cdots & \left.\dfrac{\partial \xi_i}{\partial x_j}\right|_{\xi_1, x_{[j]}} \end{vmatrix} \tag{3}$$

Here $\xi_{[m]}$ denotes a restraint wherein all ξ's (ξ_1 to ξ_k) except ξ_m are constant, while ξ_1 denotes that the variables ξ_1 to ξ_k are those that are held constant. The same notation is maintained for the variable x_i in the pertinent space (i.e., x_{k+1} to x_N). In Eq. 2 the terms ($\xi_1 \ldots \xi_k$) represent those that must be transformed in order to proceed from a $y^{(k)}$ to a $y^{(0)}$ formulation. Equation 2, can be rewritten in the form,

$$y_{ij}^{(k)} = \frac{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, \xi_k, \xi_i)}{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, x_k, x_j)} \cdot \frac{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, x_k, x_j)}{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, \xi_k, x_j)} \tag{4}$$

by using the chain rule for partial differentiation. Equation 4 can also be simplified to the form,

$$y_{ij}^{(k)} = \frac{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, \xi_k, \xi_i)}{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, x_k, x_j)} \Bigg/ \frac{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, \xi_k)}{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, x_k)} \tag{5}$$

In going from Eq. 2 to Eq. 5 we have expressed a second partial derivative of the kth Legendre transform in terms of the derivatives of the $(k-1)$th transform. Notice that the denominator no longer possesses an x_j term. This results as the presence of the x_j in the denominator Jacobian only introduces a unity term at the bottom right corner of the Jacobian; removing it causes no change in the determinant. Performing this operation k times yields an expression for the relevant partial derivative in terms of the derivatives of the basis function. Mathematically, this can be expressed by a ratio of two Jacobians, i.e.,

$$y_{ij}^{(k)} = \frac{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, \xi_k, \xi_i)}{\partial(x_1, x_2 \ldots x_{k-1}, x_k, x_j)} \Big/ \frac{\partial(\xi_1, \xi_2 \ldots \xi_{k-1}, \xi_k)}{\partial(x_1, x_2 \ldots x_{k-1}, x_k)} \tag{6}$$

Equation 6 is the same as Eq. 31 of Beegle et al. except that it is expressed in a more compact form.

Case 2: $i \leq k, j > k$

The general derivative $y_{ij}^{(k)}$ in this case would be represented mathematically as,

$$y_{ij}^{(k)} = -\left[\frac{\partial x_i}{\partial x_j}\right]_{\xi_1,\xi_2 \ldots \xi_k, x_{k+1}, \ldots x_{j-1}, x_{j+1}, \ldots x_N} \tag{7}$$

$$= \frac{\partial(\xi_1, \xi_2 \ldots \xi_k, -x_i)}{\partial(\xi_1, \xi_2, \ldots \xi_k, x_j)} \tag{8}$$

Equation 8 is similar to Eq. 2 except that the variable ξ_i has been replaced by the relevant variable in this case, namely $-x_i$. Implementing the steps used in obtaining Eqs. 3 to 6 from Eq. 2, we obtain an expression for this partial derivative in terms of the derivatives of the basis function; i.e.,

$$y_{ij}^{(k)} = \frac{\partial(\xi_1, \xi_2 \ldots, \xi_k, -x_i)}{\partial(x_1, x_2, \ldots, x_k, x_j)} \Big/ \frac{\partial(\xi_1, \xi_2, \ldots \xi_k)}{\partial(x_1, x_2 \ldots x_k)} \tag{9}$$

Equation 9 is the same as Eq. 32 of Beegle et al.

Case 3: $i \leq k, j \leq k$

$y_{ij}^{(k)}$ in this case also can be obtained by following the same techniques used in the previous two cases. Mathematically,

$$y_{ij}^{(k)} = -\left[\frac{\partial x_i}{\partial \xi_j}\right]_{\xi_1,\xi_2 \ldots \xi_{j-1},\xi_{j+1}, \ldots \xi_k, x_{k+1}, \ldots x_N} \tag{10}$$

$$= \frac{\partial(\xi_1,\xi_2 \ldots \xi_{j-1},\xi_{j+1}, \ldots \xi_k, -x_i)}{\partial(\xi_1,\xi_2, \ldots \xi_{j-1},\xi_{j+1}, \ldots \xi_k,\xi_j)} \tag{11}$$

$$y_{ij}^{(k)} = \frac{\partial(\xi_1,\xi_2 \ldots \xi_{j-1},\xi_{j+1} \ldots, \xi_k, -x_i)}{\partial(x_1,x_2, \ldots x_{j-1},x_{j+1} \ldots, x_k,x_j)} \Big/ \frac{\partial(\xi_1,\xi_2, \ldots \xi_k)}{\partial(x_1,x_2 \ldots x_k)} \tag{12}$$

This expression is the same as Eq. 33 of Beegle et al. A feature to be noted in Eq. 12 is that the numerator Jacobian is of order k, rather than $(k+1)$ as in cases 1 and 2.

Examples

Let us define for a binary mixture,

$$y^{(0)} = \underline{U} = f(\underline{S}, \underline{V}, N_1, N_2) \tag{13}$$

To illustrate the relations derived above let us express the derivative $[\partial\mu_1/\partial N_1]_{P,T,N_2}$ in terms of the derivatives of $\underline{U}$. Following standard notation, we define the following quantities:

$$x_1 = \underline{S} \quad x_2 = \underline{V} \quad x_3 = N_1 \quad x_4 = N_2,$$

$$\xi_1 = T \quad \xi_2 = -P \quad \xi_3 = \mu_1 \quad \xi_4 = \mu_2.$$

The derivative desired is thus $y_{33}^{(2)}$ in terms of the derivatives of $y^{(0)}$. This is an example of case 1, illustrated in Eqs. 2 to 5, with $i = 3, j = 3, k = 2$.

$$y_{33}^{(2)} = \left[\frac{\partial \xi_3}{\partial x_3}\right]_{\xi_1,\xi_2,x_4} = \frac{\partial(\xi_1,\xi_2,\xi_3)}{\partial(\xi_1,\xi_2,x_3)} \tag{14}$$

$$= \frac{\partial(\xi_1,\xi_2,\xi_3)}{\partial(x_1,x_2,x_3)} \Big/ \frac{\partial(\xi_1,\xi_2)}{\partial(x_1,x_2)} \tag{14a}$$

Reverting to the original notation and expressing Eq. 14a in matrix form thus yields the desired result; i.e.,

$$y_{33}^{(2)} = \frac{\begin{vmatrix} \left.\frac{\partial T}{\partial \underline{S}}\right|_{\underline{V},N_1,N_2} & -\left.\frac{\partial P}{\partial \underline{S}}\right|_{\underline{V},N_1,N_2} & \left.\frac{\partial \mu_1}{\partial \underline{S}}\right|_{\underline{V},N_1,N_2} \\ \left.\frac{\partial T}{\partial \underline{V}}\right|_{\underline{S},N_1,N_2} & -\left.\frac{\partial P}{\partial \underline{V}}\right|_{\underline{S},N_1,N_2} & \left.\frac{\partial \mu_1}{\partial \underline{V}}\right|_{\underline{S},N_1,N_2} \\ \left.\frac{\partial T}{\partial N_1}\right|_{\underline{S},\underline{V},N_2} & -\left.\frac{\partial P}{\partial N_1}\right|_{\underline{S},\underline{V},N_2} & \left.\frac{\partial \mu_1}{\partial N_1}\right|_{\underline{S},\underline{V},N_2} \end{vmatrix}}{\begin{vmatrix} \left.\frac{\partial T}{\partial \underline{S}}\right|_{\underline{V},N_1,N_2} & -\left.\frac{\partial P}{\partial \underline{S}}\right|_{\underline{V},N_1,N_2} \\ \left.\frac{\partial T}{\partial \underline{V}}\right|_{\underline{S},N_1,N_2} & -\left.\frac{\partial P}{\partial \underline{V}}\right|_{\underline{S},N_1,N_2} \end{vmatrix}} \tag{15}$$

The extension of the scheme to express the derivative $y_{ij}^{(k)}$ in terms of the derivatives of any Legendre transform is also possible. To accomplish this would entail the use of the appropriate variables while expressing the derivative in a Jacobian form. The relation would then be derived in a form analogous to either one of the three presented methods. As an example let us express the derivative $y_{33}^{(2)}$ in terms of $y_{33}^{(1)}$ (the Helmholtz energy) rather than in terms of $y^{(0)}$. Then

$$y_{33}^{(2)} = \frac{\partial(\xi_2,\xi_3)}{\partial(\xi_2,x_3)} = \frac{\partial(\xi_2,\xi_3)}{\partial(x_2,x_3)} \Big/ \frac{\partial(\xi_2)}{\partial(x_2)} \tag{16}$$

Equation 16 may be written without using matrix representation.

Let us now pick a quarternary system and again define $y^{(0)}$ as:

$$y^{(0)} = \underline{U} = f(\underline{S}, \underline{V}, N_1, N_2, N_3, N_4) \tag{17}$$

Suppose we wish to express the derivative $-[\partial N_2/\partial T]_{P,\mu_1,N_3,N_4}$ in terms of the derivatives of (a) $y^{(0)}$ and (b) $y^{(6)}$. In part (a) the required derivative is $y_{41}^{(4)}$ in terms of $y^{(0)}$. This can be accomplished by recognizing it to be a case 3 problem; i.e.,

$$y_{41}^{(4)} = -\left[\frac{\partial x_4}{\partial \xi_1}\right]_{\xi_2,\xi_3,\xi_4,x_5,x_6}$$

$$= \frac{\partial(\xi_2, \xi_3, \xi_4, -x_4)}{\partial(x_2, x_3, x_4, x_1)} \bigg/ \frac{\partial(\xi_1, \xi_2, \xi_3, \xi_4)}{\partial(x_1, x_2, x_3, x_4)} \tag{18}$$

$$= \frac{\partial(-P, \mu_1, \mu_2, -N_2)}{\partial(\underline{V}, N_1, N_2, \underline{S})} \bigg/ \frac{\partial(T, -P, \mu_1, \mu_2)}{\partial(\underline{S}, \underline{V}, N_1, N_2)} \tag{19}$$

For part (b), it is noted that the variables to be transformed in order to go from $y^{(4)}$ to $y^{(6)}$ are x_5 and x_6. This particular example can thus be identified as a case 1 problem and solved as:

$$y_{41}^{(4)} = \frac{\partial(x_5, x_6, -x_4)}{\partial(x_5, x_6, \xi_1)} = \frac{\partial(x_5, x_6, -x_4)}{\partial(\xi_5, \xi_6, \xi_1)} \bigg/ \frac{\partial(x_5, x_6)}{\partial(\xi_5, \xi_6)} \tag{20}$$

Conclusion

A method has been developed of expressing the second partial derivatives of any Legendre transform in terms of the derivatives of any other transform. The technique presented thus verifies the unproved results of Beegle et al. (1974), and allows one to obtain readily the desired results. Extension of this technique to higher order partial derivatives is possible by employing third- and higher dimension Jacobians.

Notation

N_i = number of moles of the ith component in a mixture
P = system pressure
$\underline{S}$ = total entropy of a system
T = temperature
$\underline{U}$ = total internal energy of a system
$\underline{V}$ = total system volume
x_i = variable in the basis function $y^{(0)}$
$y^{(0)}$ = Legendre transform basis function
$y^{(n)}$ = nth Legendre transform of the basis function
μ_i = chemical potential of component i in a mixture
ξ_i = congugate variable of x_i in Legendre transform representation

Literature cited

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