A Simple Method to Reduce Thermodynamic Derivatives by Computer

Jacques H. H. Perk

Department of Physics, Oklahoma State University, Stillwater, OK 74078-3072

(Dated: January 31, 2014)

Studies in thermodynamics often require the reduction of some first or second order partial derivatives in terms of a smaller basic set. A simple algorithm to perform such a reduction is presented here, together with a review of earlier related works. The algorithm uses Jacobians and is written in Maple language, but it is easily translated in terms of any other computer algebra language.

I. INTRODUCTION

About 20 years ago I was teaching a statistical thermodynamics course using the text by Rumer and Ryvkin. The students liked it very much as the book sold new for $7 only, until MIR Publishers in Moscow went out of business. From that book I learned the use of Jacobians for the reduction of partial derivatives in thermodynamics. This allowed me to create a simple Maple 5.4 algorithm to systematically do this for me. Recently, I got to teach the course again using Callen’s text which does not use Jacobians for the reduction, even though a section on it was included in the first edition.

As the Jacobian method is efficient and general, it seems worthwhile to give a historical review of the method and to present my old algorithm in Maple 16 format. It is a simple exercise to translate the code in other formats like Mathematica. At this point I must mention a Wolfram Demonstrations Project created by Mikhailov about 2009. The Mathematica source code of his CDF file is more or less equivalent to the first part of my code presented below.

Originally the reduction was done without Jacobians, and large tables were constructed from which the partial derivatives could be constructed dividing two entries from these tables, see especially the works by Bridgman and Tobolsky discussed how to amend Bridgman’s approach if other thermodynamic variables like length and tension were involved. Benn described an efficient way to reconstruct the tables from a set of linear relations among differentials.

The use of Jacobians in the current context goes back to at least the early 1900s, see the encyclopedia article by Bryan where in (78)–(82) he indicated how for a single-component system all partial derivatives can be reduced in terms of those with two given independent variables. Two of his equations involve Jacobians and in footnote 57 he attributes this in part to earlier work by Rankine as the Jacobians arise as the ratio of the areas of two infinitesimal parallelograms related by a change of variables. Bryan also discusses the Jacobian approach in his textbook but he does not go into enough applications to demonstrate its usefulness.

Shaw used Jacobians to extend the Bridgman tables also providing a new big table for the reduction of second derivatives. His Jacobian approach for first derivatives reproduces the results of Bridgman and he organized these also in one huge table. But unless one uses his tables regularly and is very familiar with them, one may prefer to derive the results oneself using the Jacobian method, as advocated by Crawford and Pinkerton.

The efficiency of the Jacobian approach has been claimed by various other authors and in textbooks like the ones of Tribus, Landau and Lifshitz, and Jaynes.

The case of three or more independent variables has also been addressed in the Jacobian approach.

Finally, some authors have sought to implement the reduction method based on Jacobians using computers. In the mid 1980s Farah and Missen used muMath, a list-processing language like LISP. Very recently Cooper described an implementation using Mathematica that seems more complicated than needed, also involving Gröbner bases. The only simple implementation seems to be the Mathematica app created by Mikhailov mentioned above. The code presented below does more, however, as it also addresses second derivatives and can be generalized in various directions including third or higher derivatives or more independent variables.

II. JACOBIANS

Even though the properties of Jacobians have been reviewed in several of the above citations, it may be good to summarize them here. A Jacobian is defined as the determinant of first derivatives:

\[ D = \frac{\partial (x_1, x_2, \ldots, x_n)}{\partial (y_1, y_2, \ldots, y_n)} = \begin{vmatrix} \frac{\partial x_1}{\partial y_1} & \frac{\partial x_1}{\partial y_2} & \cdots & \frac{\partial x_1}{\partial y_n} \\ \frac{\partial x_2}{\partial y_1} & \frac{\partial x_2}{\partial y_2} & \cdots & \frac{\partial x_2}{\partial y_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial x_n}{\partial y_1} & \frac{\partial x_n}{\partial y_2} & \cdots & \frac{\partial x_n}{\partial y_n} \end{vmatrix}. \] (1)

Jacobian satisfies the following fundamental properties:

1. Antisymmetry: A Jacobian is fully antisymmetric under the exchange of rows or columns, e.g.,

\[ \frac{\partial (x_1, \ldots, x_j, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} = - \frac{\partial (x_1, \ldots, x_j+1, x_j, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} , \]

\[ \frac{\partial (x_1, \ldots, x_j, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} = - \frac{\partial (x_1, \ldots, x_j, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} = \frac{\partial (x_1, \ldots, x_j, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} . \]
\[
\frac{\partial (x_1, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} = - \frac{\partial (x_1, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} \tag{2}
\]
which together generate the full antisymmetry.

2. Multiplication:
\[
\frac{\partial (x_1, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} = \frac{\partial (x_1, \ldots, x_n)}{\partial (z_1, \ldots, z_n)} \frac{\partial (z_1, \ldots, z_n)}{\partial (y_1, \ldots, y_n)} \tag{3}
\]
which is a direct consequence of the chain rule
\[
\frac{\partial z_1}{\partial y_j} = \sum_k^{n} \frac{\partial x_k}{\partial z_k} \frac{\partial z_k}{\partial y_j}
\]
and \( \det AB = \det A \det B \).

3. Reciprocity:
\[
\frac{\partial (x_1, \ldots, x_n)}{\partial (y_1, \ldots, y_n)} \frac{\partial (y_1, \ldots, y_n)}{\partial (x_1, \ldots, x_n)} = 1, \tag{4}
\]
following from multiplication and \( \frac{\partial x_i}{\partial x_j} = \delta_{ij} \), (which is 1 if \( i = j \) and 0 if \( i \neq j \)).

4. Reduction: Again using \( \frac{\partial x_i}{\partial x_j} = \delta_{ij} \), we have
\[
\frac{\partial (y_1, \ldots, y_m, x_{m+1}, \ldots, x_n)}{\partial (x_1, \ldots, x_m, x_{m+1}, \ldots, x_n)} = \frac{\partial (y_1, \ldots, y_m)}{\partial (x_1, \ldots, x_m)} \bigg|_{x_{m+1}, \ldots, x_n=\text{const}}. \tag{5}
\]
For example,
\[
\begin{vmatrix}
\frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \cdots & \frac{\partial y_1}{\partial x_n} \\
0 & 1 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & 1
\end{vmatrix}
= \left( \frac{\partial y_1}{\partial x_1} \right)_{x_2, \ldots, x_n}. \tag{6}
\]

These properties mean that we can treat the \( \partial (x_1, x_2, \ldots, x_n) \) formally as if they are numbers. More precisely, we can define
\[
J(x_1, x_2, \ldots, x_n) = \frac{\partial (x_1, x_2, \ldots, x_n)}{\partial (b_1, b_2, \ldots, b_n)}, \tag{7}
\]
for a given preferred basic set of independent variables \( b_1, b_2, \ldots, b_n \). Then,
\[
\frac{\partial (x_1, x_2, \ldots, x_n)}{\partial (y_1, y_2, \ldots, y_n)} = \frac{J(x_1, x_2, \ldots, x_n)}{J(y_1, y_2, \ldots, y_n)}, \tag{8}
\]
which also explains how the original work of Bridgman works.\(^3\)

The above properties imply also the well-known minus-one and plus-one rules often used in thermodynamics:

5. Minus-one rule: If \( f(x, y, z) = 0 \), then
\[
\left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = \frac{\partial (x, z)}{\partial (y, z)} \frac{\partial (y, x)}{\partial (z, x)} \frac{\partial (z, y)}{\partial (x, y)} = -1. \tag{9}
\]

6. Plus-one rule: If \( f(x, y, z, u) = 0 \) and \( g(x, y, z, u) = 0 \), then two of \( x, y, z, u \) are fixed if the other two are specified. Then any pair can be considered as the independent variables, so that
\[
\left( \frac{\partial x}{\partial y} \right)_u \left( \frac{\partial y}{\partial z} \right)_u = \frac{\partial (x, u)}{\partial (y, u)} \frac{\partial (y, u)}{\partial (z, u)} \frac{\partial (z, u)}{\partial (x, u)} = +1. \tag{10}
\]
Finally, Jacobians can also be used as a condition for exact differentials.

7. Exact differential: The following are equivalent:
\[
df = \sum_{j=1}^{n} f_j \, dx_j \quad \text{exact differential}
\iff \int_A^B df = 0
\iff \int_A^B df \quad \text{path independent}
\iff f_j = \frac{\partial f}{\partial x_j}
\iff \int_A^B df_i = \frac{\partial f_i}{\partial x_j}
\iff \int_A^B df_j = \frac{\partial (f_1, x_1)}{\partial (f_j, x_j)} = -1, \tag{11}
\]
as the last equality implies \( \frac{\partial (f_1, x_1)}{\partial (x_1, x_1)} = \frac{\partial (f_1, x_1)}{\partial (x_j, x_j)} \), which is the line above it. The other equivalences are also fundamental in junior and higher level mechanics and electromagnetism courses, to which we can refer.

III. MAPLE IMPLEMENTATION

Consider a one-component system with a fixed amount of \( N \) moles of matter. We want to simplify all first and second partial derivatives involving the following eight variables: absolute temperature \( T \), entropy \( S \), pressure \( P \), volume \( V \), and the four thermodynamic potentials \( U, H, F \) (also denoted \( A \) at times) and \( G = N \mu \) (with \( \mu \) the chemical potential),
\[
U = U(S, V, N), \quad dU = TdS - PdV + \mu dN,
H = H(S, P, N), \quad dH = TdS + VdP + \mu dN,
F = F(T, V, N), \quad dF = -SdT - PdV + \mu dN,
G = G(T, P, N), \quad dG = -SdT + VdP + \mu dN. \tag{12}
\]
In the Maple code we formally replace $\partial(X, Y)$, with $X$ and $Y$ chosen from the list of eight variables, by $J[n[X], n[Y]]$, where $n$ replaces each variable's symbol by a number from 1 to 8. From the antisymmetry of $J[i,j]$ and $J[j,i]$ we can now construct the code for the first derivatives, provided we express four of the derivatives in terms of the isobaric thermal volume expansion coefficient $\alpha$, the two specific heats $c_p$ and $c_v$ and the isothermal compressibility $\kappa_T$, namely

$$ap = \alpha = \alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p,$$

$$cp = C_p/N = c_p = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_p,$$

$$cv = C_v/N = c_v = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_v,$$

$$kt = \kappa = \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T. \quad (13)$$

It may be noted that in many textbooks $\alpha$ is used for the linear expansion coefficient and $\beta$ for the volume one, but this notation is found in statistical physics due to the ubiquitous use of $\beta = 1/k_B T$.

We can now give the first part of the Maple code:

```maple
k:=normal(J[1,1]/J[1,2]):
for j to 8 do J[j,j]:=0; end do:
end do:
d:=proc(x,y,z) local a,ct,k,o; global m,su;
d:=pcal(x,y,z)
for i from 4 to 8 do J[i,i]:=T*J[i,i]-P*J[i,3];
J[6,3]:=T*J[6,3]+V*J[1,3];
J[7,3]:=S*J[7,3]-P*J[3,3];
J[8,3]:=S*J[2,3]+V*J[1,1]
end do:
for i from 6 to 8 do for j from 5 to i-1 do
J[i,j]:=J[j,i]+J[i,3]*J[j,3]/J[1,3]
end do;
end do:
for k to 8 do a:=a+diff(o, m[k])*ct(m[k]);
a:=simplify(a) RETURN(a) end proc:
```

One can add further code to eliminate $S_T, S_{TT},$ etc., in terms of $\alpha, c_p, \kappa_T$ and their first derivatives, if so desired. Now “dd(X,Y,Z)” works out $\frac{\partial^2 F}{\partial X \partial Y}$ with $X$ a fairly general expression and $Y$ and $Z$ taken from the list of eight. $T$ through $G$, but with $Y$ and $Z$ not the same. In general, the results can be quite messy.

To give an example, “dd(d(F,S,P),T,P)” gives

$$\left( \frac{\partial^2 F}{\partial T \partial S} \right)_P = -\frac{PS_T V_{TT} - PV_T S_{TT} + S_T^2 - S_{TT}}{S_T^2},$$

which can be processed further, as $S_T = Nc_p/T, V_T = V\alpha_p$, etc. Some of this processing can be done by making additions to the above code, but this will depend on possible applications one has in mind.

IV. FINAL REMARKS

In the previous section we started with $G(T, P, N)$ with $N$ fixed and with $T$ and $P$ as the pair of independent variables. Alternatively we could have started with one of three other thermodynamic potentials, $U(S, V, N), H(S, P, N), or F(T, V, N).$ This leads to three variations of the previous section with three different second and four different third derivatives of the other thermodynamic potential with respect to its own pair of independent variables.

It is also straightforward to extend the code to higher derivatives, the way the previous section is set up. Next, another variation is to replace $P$ by magnetic field $B$ and $V$ by magnetization $M$. One can also treat the various entropic versions, which are more directly related to the various statistical-mechanical ensembles as the role of $S$ and $U$ is interchanged.
In order to treat cases of thermodynamic potentials with three of more independent variables, one must let the $J$ of the previous section depend on three or more integers. An example is starting with $G(T,P,x,N)$ for a two-component system with $N_1 = xN$ and $N_2 = (1-x)N$ moles of the two components and total amount $N$ fixed. The code can be worked out, but it will be much more elaborate.

Finally, it is an easy exercise to implement the above codes in other computer languages like Mathematica.

**ACKNOWLEDGMENTS**

This work has been supported in part by the National Science Foundation under grant No. PHY-07-58139.

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