Mathematical Physics II

PHYS 502

Problem Set # 7
Distributed February 19, 2016
Due March 2, 2016
Linear Stuff

1. Linear Constraints: If constraints are placed on independent variables u, v, w, x, y, z they are no longer independent. Three constraints are placed on five variables as follows:

$$\begin{array}{rcl} u & = & Bw + Cv \\ w & = & Dx + Ey \\ v & = & E'x + Fy \end{array} \tag{1}$$

This means that the five variables are no longer independent. There are now only two *independent* variables. They can usually be chosen at your convenience. In these expressions $B, C, D, \cdots$ can be treated as constants and therefore the constraints are linear.

Choose w, x as independent variables and write the others as (linear) functions of these two variables. As usual, it is convenient to represent the linear relations in matrix form:

$$\left[\begin{array}{c} u \\ v \\ y \end{array}\right] = \left[\begin{array}{cc} M_{11} & M_{12} \\ M_{21} & M_{22} \\ M_{31} & M_{32} \end{array}\right] \left[\begin{array}{c} w \\ x \end{array}\right] \tag{2}$$

a. Construct this matrix.

2. Local Constraints: Sometimes the variables describe points on a curved surface, so they no longer have linear properties. In such cases Physicists resort to "*infinitesimalization*" and replace the 'global' coordinates by local coordinates: *i.e.,* differentials, so the relations above become

$$
\begin{array}{rcl}
du & = & Bdw + Cdv \\
dw & = & Ddx + Edy \\
dv & = & E'dx + Fdy
\end{array} \tag{3}
$$

Choose dw, dx as independent infinitesimal displacements and write the others as (linear) functions of these two differentials. As usual, it is convenient to represent the linear relations in matrix form:

$$
\left[\begin{array}{c} du \\ dv \\ dy \end{array}\right] = \left[\begin{array}{cc} M_{11} & M_{12} \\ M_{21} & M_{22} \\ M_{31} & M_{32} \end{array}\right] \left[\begin{array}{c} dw \\ dx \end{array}\right] \tag{4}
$$

a. Convince yourself (and me!) that

$$
\left[\begin{array}{cc} M_{11} & M_{12} \\ M_{21} & M_{22} \\ M_{31} & M_{32} \end{array}\right] = \left[\begin{array}{cc} \left(\dfrac{\partial u}{\partial w}\right)_x & \left(\dfrac{\partial u}{\partial x}\right)_w \\ \left(\dfrac{\partial v}{\partial w}\right)_x & \left(\dfrac{\partial v}{\partial x}\right)_w \\ \left(\dfrac{\partial y}{\partial w}\right)_x & \left(\dfrac{\partial y}{\partial x}\right)_w \end{array}\right] \tag{5}
$$

Interpret the symbology for me.

3. Application: The First Law of Thermodynamics (closed system, reversible transformation) says

$$
dU = TdS - PdV \tag{6}
$$

Linear response functions relate infinitesimal changes in conjugate extensive and intensive variables:

$$
\left[\begin{array}{c} dS \\ dV \end{array}\right] = \left[\begin{array}{cc} D & E \\ E' & F \end{array}\right] \left[\begin{array}{c} dT \\ -dP \end{array}\right] \tag{7}
$$

The matrix elements can be determined by arguments like $dS = E(-dP)_T \Rightarrow E = -\left(\frac{\partial S}{\partial P}\right)_T = -\frac{1}{T}\left(T\left(\frac{\partial S}{\partial P}\right)_T\right) = -\frac{1}{T}\Gamma_T$, where Γ_T is the heat of pressure variation at constant temperature. Other linear response coefficients you will encounter are α (thermal expansion coefficients), β (compressibilities), and C (specific heats).

a. Compute the remaining linear response functions for me.

b. Argue that, since U is a potential, $E' = E$. This prediction can be tested by comparing the corresponding two linear response functions with each other. What were the results?

c. Identify the variables x, y, z, u, v, w and coefficients $A, B, C, D \cdots$ in Problems 1 and 2 with the physical quantities $U, S, V, T, -P, \cdots$ in this problem. Standardize with $dw = dS$.

d. A number of thermodynamic texts claim that you cannot compute thermodynamic partial derivatives for which a conjugate pair of variables is chosen as independent. Show that such claims are hogwash by computing

$$\left(\frac{\partial \text{ (anything)}}{\partial T} \right)_S$$

4. Equalities and Inequalities: Another set of linear response functions relates changes in intensive quantities to changes in extensive quantities:

$$\begin{bmatrix} dT \\ -dP \end{bmatrix} = \begin{bmatrix} G & H \\ H' & J \end{bmatrix} \begin{bmatrix} dS \\ dV \end{bmatrix} \tag{8}$$

a. Compute these four linear response functions using the technology advanced in Problem #3.

b. Convince me that $H = H'$.

c. How are the matrices of linear response functions in Problems 3 and 4 related?

d. Multiply them together to obtain a suite of thermodynamic equalities.

e. Both matrices are positive definite. This means the products of eigenvalues (*e.g.,* a determinant) are always positive. Use this information to construct some thermodynamic *inequalities.*

Remark: The matrix elements of linear response functions are *second derivatives* of the thermodynamic potential $U = U(S, V)$ with respect to its variables. These matrix elements therefore measure the *curvature* of the equilibrium surface. The matrices of linear response functions are in fact matrices of second partial derivatives of the thermodynamic potential. The thermodynamic potential itself is concave upwards. This requires the mixed second partial derivatives to be positive definite (also its inverse) and to obey various equalities and inequalities.