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# On the solutions of the Gibbs–Duhem equation

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**Abstract.** According to the classical thermodynamic description, a coexistence surface results from the intersection of the hypersurfaces which are the solutions of the Gibbs–Duhem (GD) equations for each single coexisting phase. This geometrical view is not thermodynamically consistent in that it conventionally relies on the introduction of the metastable extension of the one-phase equilibrium surfaces. It is shown that a new, fully consistent thermodynamic description is possible. Our approach is characterised by a local study of the solutions of the GD equation, regarded as a differential equation in the contact space in which all the densities and fields are regarded as independent variables. An  $m$ -phase solution is described as one in which  $(m - 1)$  densities may be fixed arbitrarily and the others are linear functions of these. The Gibbs phase rule is found to be valid for these solutions, although in no way can they be regarded as resulting from the intersection of single-phase solutions. Changes of variables in thermodynamics are identified with contact transformations leaving the fundamental equation invariant.

## 1. Introduction

The classical discussion of phase equilibrium within the framework of thermodynamics is that given by Gibbs (1876). It is based on the Gibbs–Duhem (GD) equation which, for a multicomponent fluid system, may be written as

$$-V dp + S dT + N_1 d\mu_1 + \dots + N_c d\mu_c = 0 \quad (1.1)$$

or, in terms of intensive variables,

$$dp = \sigma dT + \rho_1 d\mu_1 + \dots + \rho_c d\mu_c \quad (1.2)$$

where

$$\sigma = S/V \quad \text{and} \quad \rho_i = N_i/V \quad (i = 1, 2, \dots, c).$$

When written in the form (1.2) the GD equation is regarded as the differential expression of a *fundamental equation* (Gibbs 1876)

$$p = p(T, \mu_1, \dots, \mu_c) \quad (1.3)$$

which is interpreted geometrically as a  $(c + 1)$ -dimensional hypersurface in the  $(c + 2)$ -dimensional *extended field space* described by the fields (Griffiths and Wheeler 1970)  $T$ ,  $\mu_i$  and  $p$ .

Different phases in equilibrium are characterised by different values for the density variables  $\sigma$ ,  $\rho_i$  but identical values for the fields. Since the densities are defined as partial derivatives of equation (1.3) a coexistence surface is naturally regarded as

resulting from the intersection in the extended field space of the  $(c + 1)$ -dimensional hypersurfaces which are the solutions of the GD equations for each single phase of the system.

Following this view, the most important result of the thermodynamics of phase equilibria, namely the Gibbs phase rule, appears as the translation in thermodynamic language of geometrical properties concerning the intersection of surfaces in multi-dimensional spaces. For example, the coexistence of four phases for a single-component system is excluded on the basis that the intersection at the same point of four surfaces is to be considered a highly improbable event (Gibbs 1876, Griffiths and Wheeler 1977, private communication).

This geometrical view of phase coexistence, although attractive and heuristically powerful, should be regarded as conventional in that it relies on the introduction of the 'metastable' extension of the one-phase equilibrium surfaces. Even if this description is not physically absurd, since metastable states have been realised in most cases, their description lies outside the strict province of equilibrium thermodynamics and for this reason it has for some time been seriously criticised in the literature (Pippard 1966, Wheeler 1974) but, to the author's knowledge, no alternative approach has been proposed so far.

Moreover, in practical terms difficulties arise when the primary experimental information is the coexistence locus, the shapes of the single-phase hypersurfaces being inaccessible in the immediate neighbourhood of the locus. With this in mind, we propose in this paper an alternative, fully consistent thermodynamic description of multiphase equilibrium through the analysis of all possible solutions of the GD equation. Indeed, in deriving this equation from the laws of thermodynamics we do not need to assume that a single-phase system is considered so that the same single equation should be used to describe all possible states of a given system irrespective of the number of phases. Rather than the discontinuity of the densities at the coexistence surface, which is central to the classical, phase-based concept, we may look at the behaviour of the average densities of the system, some of which may be chosen arbitrarily within given limits in the coexistence region, while the others are linear functions of these. Let us consider, for example, a one-component system in a two-phase region. The two phases will be referred to as  $\alpha$  and  $\beta$  and the phase  $\alpha$  will be assumed to be the more dense. Then, with obvious notation, we have for the average densities of the system

$$\rho = x\rho^\alpha + (1-x)\rho^\beta \quad \epsilon = x\epsilon^\alpha + (1-x)\epsilon^\beta \quad \sigma = x\sigma^\alpha + (1-x)\sigma^\beta \quad (1.4)$$

where  $\epsilon$  denotes the internal energy density and  $x = V^\alpha/V$ . Solving now for  $x$  from the first of these equations we get

$$x = (\rho - \rho^\beta)/(\rho^\alpha - \rho^\beta) \quad (1.5)$$

and therefore

$$\epsilon = \frac{\epsilon^\beta - \epsilon^\alpha}{\rho^\beta - \rho^\alpha} \rho + \frac{\rho^\beta \epsilon^\alpha - \rho^\alpha \epsilon^\beta}{\rho^\beta - \rho^\alpha} \quad \sigma = \frac{\sigma^\beta - \sigma^\alpha}{\rho^\beta - \rho^\alpha} \rho + \frac{\rho^\beta \sigma^\alpha - \rho^\alpha \sigma^\beta}{\rho^\beta - \rho^\alpha}; \quad (1.6)$$

that is, the internal energy  $\epsilon$  and the entropy density  $\sigma$  are expressed as linear functions of  $\rho$  for  $\rho$  within the interval  $(\rho^\beta, \rho^\alpha)$ .

This linear relation between densities will in turn imply a constraint on the fields so that the coexistence surfaces in the field space will have a dimensionality in agreement with the Gibbs phase rule, although there is no need to interpret them as resulting from

the intersection of single-phase solutions. It will be shown in the next section that all the coexistence surfaces, irrespective of the number of phases, will appear as projections on the field space of  $(c + 1)$ -dimensional solutions of the GD equation.

In this way we obtain a unified representation of both single and multiphase equilibrium states in which the validity of the phase rule appears as the result of a projection operation rather than an intersection.

Equation (1.1) is not a single homogeneous form which can be identified with the GD equation. Working in the entropy scheme (Tisza 1961) one would obtain

$$U d(1/T) + V d(\rho/T) - \sum_{i=1}^c N_i d(\mu_i/T) = 0 \quad (1.7)$$

and the corresponding equation in term of intensive variables is obtained by dividing, for example, by  $RV$ , where  $R$  is the gas constant to obtain the form (Leung and Griffiths 1973)

$$d\omega = \sum_{i=1}^c \rho_i d\nu_i - \epsilon dB \quad (1.8)$$

where

$$\omega = \rho/RT \quad \nu_i = \mu_i/RT \quad (i = 1, 2, \dots, c) \quad B = 1/RT.$$

It is an essential feature of most presentations of thermodynamics to point out that the same information can be given in many different ways by changing the set of variables. The choice of the method of representation is, of course, to a large extent arbitrary and is determined in any particular case by some criterion of convenience and simplicity. In such a situation we have to know how various objects change when we change coordinates. Variable transformations which leave the GD equation invariant as well as their effect on its solutions will be discussed in § 3. There we will also point out the relevance of projective transformations for the interpretation of certain aspects of phase diagrams.

## 2. Coexistence surfaces as solutions of the GD equation

A uniform notation will be convenient in the following, and therefore we introduce  $\rho_0 \equiv \sigma$  and  $\mu_0 \equiv T$  so that the GD equation in the non-homogeneous form (1.2) becomes

$$dp - \rho_i d\mu_i = 0 \quad (2.1)$$

where the summation sign will be omitted in expressions like this unless confusion might result.

It is often quite convenient, and it is indeed a fairly general procedure for the study of a physical system, to start with a representation of the *states* of that system, by means of the *points* of a suitable space. For example, the *microscopic state* of a system is described in classical Hamiltonian mechanics by means of a point in phase space. This classical phase space is a differentiable manifold of even dimensionality, obviously very large for any macroscopic system, endowed with a symplectic structure, i.e. a regular and closed two-form. By contrast, the *macroscopic state* of a system, i.e. its thermodynamic state, is described by means of a small number of measurable physical quantities which, for this reason, are usually called *variables or parameters of states*. For

a  $c$ -component fluid system we need  $(c + 1)$  independent variables. Often one starts with a space spanned by  $(c + 1)$  fields, the *field space*; however, as we have discussed in the previous section, in a multiphase region we have to regard the densities as well as the fields as independent variables and it is most convenient, for the interpretation of the results we will obtain in this section, to define a state by means of  $(2c + 3)$  quantities, namely the  $(c + 1)$  pairs  $(\mu_i, \rho_i)$  and  $p$ .

We may regard a state as a point in a  $(2c + 3)$ -dimensional space, the states space. In this space, of odd dimensionality, equation (2.1) defines at each point a tangent hyperplane of even dimensionality  $2(c + 1)$ . This field of hyperplanes is nondegenerate and provides, therefore, the state space with a *contact structure* (see appendix). We may call a states space in which a contact structure is defined by means of a GD equation in the nonhomogeneous form (2.1) a *contact space*. It is a fortunate circumstance that this terminology, introduced here in conformity with mathematical conventions dating back to Lie (Eisenhart 1961), is also meaningful from a purely thermodynamic point of view. Indeed, the number and type of variables which enter in the definition of a contact space for a thermodynamic system are obviously related to the number and type of energetic contacts, defined through suitable *walls*, that the system can have.

A solution of the GD equation is any integral hypersurface of the field of hyperplanes in the contact space, namely a submanifold such that at each point its tangent plane belongs to the hyperplane defined by Eq. (2.1). In order to classify all possible solutions it is most appropriate to start with a parametric representation. Let

$$\begin{aligned} \mu_i &= \mu_i(x_1, \dots, x_n) \\ \rho_i &= \rho_i(x_1, \dots, x_n) \quad n < 2(c + 1) \\ p &= p(x_1, \dots, x_n) \end{aligned} \tag{2.2}$$

be the parametric equations of a solution. We cannot have  $n = 2(c + 1)$ , for the field of hyperplanes, defined through the GD *contact form* on the RHS of equation (2.1), is nonintegrable in the contact space (see appendix). Consider then the equations

$$\mu_i = \mu_i(x_1, \dots, x_n) \quad (i = 0, 1, \dots, c) \tag{2.3}$$

and denote by  $f$  the rank of the jacobian

$$\frac{\partial(\mu_0, \mu_1, \dots, \mu_c)}{\partial(x_1, x_2, \dots, x_n)} \tag{2.4}$$

This number,  $f$ , which can also be zero if all the functions (2.3) are constant, can exceed neither the number  $n$  nor the number  $(c + 1)$ . It is always possible to relabel the indices of the  $(\mu_i, \rho_i)$  and the  $x_K$  such that the  $f$  first equations (2.3) are solvable for  $x_1, x_2, \dots, x_f$ . If we now describe all the functions (2.2) with the help of the new variables

$$\mu_0, \mu_1, \dots, \mu_{f-1} \quad x_f, \dots, x_n \tag{2.5}$$

then  $\mu_f \dots \mu_c$ , because of our assumption concerning the rank of (2.4), become functions of  $\mu_0 \dots \mu_{f-1}$  alone and the same also holds for  $p$  if equation (2.1) is satisfied. Moreover, this last relation implies

$$\rho_i = \partial p / \partial \mu_i - \sum_{j=f}^c \rho_j \partial \mu_j / \partial \mu_i \quad (i = 0, 1, \dots, f - 1). \tag{2.6}$$

Thus we only need to know  $(\rho_f, \dots, \rho_c)$  as functions of the variables (2.5) in order to calculate all the densities. Now if  $(m - 1)$  is the rank of the jacobian

$$\partial(\rho_f, \dots, \rho_c) / \partial(x_f, \dots, x_n) \tag{2.7}$$

we can again choose the indices such that among the equations

$$\rho_J = \rho_J(\mu_0, \dots, \mu_{f-1}, x_f \dots x_n) \quad (J = f, f + 1, \dots, c) \tag{2.8}$$

the first  $(m - 1)$  are solvable for  $(x_f \dots x_{f+m-2})$ . We can then always represent the functions  $\rho_{f+m-1} \dots \rho_c$  and therefore also the hypersurface (2.2) with the help of the  $(f + m - 1)$  variables

$$\mu_0, \mu_1, \dots, \mu_{f-1} \quad \rho_f, \rho_{f+1}, \dots, \rho_{f+m-2}. \tag{2.9}$$

Obviously we always have  $n = f + m - 1 \leq c + 1$ , from which it follows that the dimension of the hypersurface (2.2) can at most be equal to  $(c + 1)$ . The most important case is that in which the dimension of the hypersurface is maximal and therefore the Gibbs phase rule  $f = c - m + 2$  is satisfied. These integral hypersurfaces with largest dimensionality are called *Legendre submanifolds* of the contact space. They can be classified according to the value taken by either  $f$  or  $m$ , respectively called the number of degrees of freedom and the number of coexisting phases.

Consider first the case specified algebraically by setting  $f = c + 1$ . In this case  $m = 1$  and equations (2.6) take the form

$$\rho_i = \partial p / \partial \mu_i \quad (i = 0, 1, \dots, c), \tag{2.10}$$

and this is a single-phase solution for the densities are determined uniquely by equations (2.10) in the neighbourhood of each point in the extended field space. In this case we may regard the last of the parametric equations (2.2), namely

$$p = p(\mu_0, \dots, \mu_c), \tag{2.11}$$

as the equation of the surface which is obtained by projecting, parallel to the  $\rho_i$  axes, the Legendre submanifold on the extended field space.

Not all single-phase solutions will represent equilibrium states; for this purpose, i.e. to represent only equilibrium states, the function  $p$  given by equation (2.11) has to be convex, and therefore we must have

$$(\partial \rho_i / \partial \mu_i) \geq 0 \quad \partial(\rho_i, \rho_j) / \partial(\mu_i, \mu_j) \geq 0 \dots \partial(\rho_{i_0}, \dots, \rho_{i_c}) / \partial(\mu_{i_0}, \dots, \mu_{i_c}) \geq 0. \tag{2.12}$$

If, however, we set  $f < c + 1$ , then  $c + 2 - f = m > 1$  and

$$\begin{aligned} p &= p(\mu_0, \dots, \mu_{f-1}) \\ \mu_{f+l} &= \mu_{f+l}(\mu_0, \dots, \mu_{f-1}) \end{aligned} \quad (l = 0, 1, \dots, m - 2) \tag{2.13}$$

and from equations (2.6)

$$\rho_i = \partial p / \partial \mu_i - \sum_0^{m-2} \rho_{f+l} \frac{\partial \mu_{f+l}}{\partial \mu_i} \quad (i = 0, 1, \dots, f - 1). \tag{2.14}$$

We then have what we may call an  $m$ -phase solution. Indeed, in this case we may arbitrarily fix the values of  $(m - 1)$  densities  $\rho_f \dots \rho_{f+m-2}$ , within given limits, and then all the other densities are determined as linear functions of these as well as  $f$  independent fields  $\mu_0, \dots, \mu_{f-1}$ , by equations (2.14). Here again not all  $m$ -phase solutions

should satisfy convexity conditions similar to those written above for a single-phase solution, namely

$$(\partial \rho_i / \partial \mu_i) \geq 0 \quad \partial(\rho_i, \rho_j) / \partial(\mu_i, \mu_j) \geq 0 \dots \partial(\rho_{i0}, \dots, \rho_{if-1}) / \partial(\mu_{i0}, \dots, \mu_{if-1}) \geq 0 \quad (2.15)$$

where the remaining  $(m - 1)$  densities  $\rho_f \dots \rho_c$  are held constant in these derivatives. In this case equations (2.13) are the parametric equations of the coexistence surface in the extended field space. Analogues of the Clausius–Clapeyron equation are readily obtained from equation (2.14).

Let us consider, for example, a two-phase equilibrium in a single-component system ( $c = 1, m = 2$ ). It will be described by a solution of the GD equation

$$dp = \sigma dT + \rho d\mu \quad (2.16)$$

in either of the two forms

$$p = p(T) \quad \mu = \mu(T) \quad \text{with } (\partial \sigma / \partial \rho)_T = -d\mu/dT \text{ and } (\partial \mu / \partial \rho)_T = 0 \quad (2.17)$$

$$\sigma = \frac{dP}{dT} - \rho \frac{d\mu}{dT}$$

or

$$p = p(\mu) \quad T = T(\mu) \quad \text{with } (\partial \rho / \partial \sigma)_\mu = -dT/d\mu \text{ and } (\partial T / \partial \sigma)_\mu = 0. \quad (2.18)$$

$$\rho = \frac{dP}{d\mu} - \sigma \frac{dT}{d\mu}$$

The convexity requirements reduce in this simple case to

$$\left( \frac{\partial \sigma}{\partial T} \right)_\rho = \frac{d^2 p}{dT^2} - \rho \frac{d^2 \mu}{dT^2} > 0 \quad (2.19)$$

and

$$\left( \frac{\partial \rho}{\partial \mu} \right)_\sigma = \frac{d^2 p}{d\mu^2} - \sigma \frac{d^2 T}{d\mu^2} > 0. \quad (2.20)$$

If in equation (2.17)  $\rho$  ranges between  $\rho^\beta$  and  $\rho^\alpha$ , the densities of the two coexisting phases, then the corresponding values of  $\sigma$  are given by the equations

$$\begin{aligned} \sigma^\alpha &= \frac{dP}{dT} - \rho^\alpha \frac{d\mu}{dT} \\ \sigma^\beta &= \frac{dP}{dT} - \rho^\beta \frac{d\mu}{dT}. \end{aligned} \quad (2.21)$$

On the other hand, these two equations can be solved for  $dP/dT$  and  $d\mu/dT$  to obtain two possible forms of the Clausius–Clapeyron equation

$$\begin{aligned} \frac{dP}{dT} &= \begin{vmatrix} \sigma^\alpha & -\rho^\alpha \\ \sigma^\beta & -\rho^\beta \end{vmatrix} / \begin{vmatrix} 1 & -\rho^\alpha \\ 1 & -\rho^\beta \end{vmatrix} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} \\ \frac{d\mu}{dT} &= \begin{vmatrix} 1 & \sigma^\alpha \\ 1 & \sigma^\beta \end{vmatrix} / \begin{vmatrix} 1 & -\rho^\alpha \\ 1 & -\rho^\beta \end{vmatrix} = -\frac{\sigma^\alpha - \sigma^\beta}{\rho^\alpha - \rho^\beta} \end{aligned} \quad (2.22)$$

where  $v$  and  $s$  denote the specific volume and entropy. The following remark is appropriate at this point. According to Gibbs' view of phase equilibrium it is possible, although entirely improbable, to imagine a situation in which three different phases, say  $\alpha$ ,  $\beta$  and  $\gamma$ , coexist along a line in the field space for a single-component system<sup>†</sup>. In this case we shall have three equations like equation (2.21) and for their simultaneous solution we should have

$$\begin{aligned}\rho^\gamma &= \lambda\rho^\alpha + \nu\rho^\beta \\ \sigma^\gamma &= \lambda\sigma^\alpha + \nu\sigma^\beta\end{aligned}\tag{2.23}$$

with  $\lambda + \nu = 1$ , namely the third phase will belong to the line segment (one-simplex) determined in the density space by the two other phases  $\alpha$  and  $\beta$ . Situations of this type do not correspond to a different solution of the GD equation and cannot be described from our local, purely thermodynamic point of view.

In general, in many ways we may obviously regard the  $f$ -dimensional coexistence surface represented by equations (2.13) in the extended field space as resulting from the intersection of  $m$  (or more for non-general positions)  $(c + 1)$ -dimensional hypersurfaces of equation

$$p = p_\alpha(\mu_0, \dots, \mu_c).\tag{2.24}$$

This possibility simply arises from dimensional considerations. We must recall, however, that an  $f$ -dimensional coexistence surface in the extended field space is obtained by projecting, parallel to the density axes, the hypersurface which is an  $m$ -phase solution of the GD equation in the  $(2c + 3)$ -dimensional contact space. Now this hypersurface will always be  $(c + 1)$ -dimensional no matter what the value of  $m$  and therefore in no way may be regarded as resulting from the intersection of  $m$  single-phase solutions. In particular, when  $f = 0$  we have  $m = c + 2$ ; then all  $\mu_i$  and  $p$  are constant and the  $\rho_i$  are arbitrary variables. In this case the  $(c + 1)$ -dimensional coexistence surface in the contact space is parallel to the densities hyperplane and its projection on the extended field space reduces to a single point.

As we remarked above, as well as the Legendre submanifolds which verify the Gibbs phase rule, there are solutions of the GD equation in which, for a given number of degrees of freedom, the number of phases is less than predicted by the phase rule, namely  $m < c + 2 - f$ . In any case, since  $f \geq 0$ , the maximum possible number of coexisting phases is always  $c + 2$ .

### 3. Change of variables in thermodynamics

In the previous section we have obtained all possible solutions of the GD equation (2.1) working in a particular coordinate system. In this local coordinate system the pressure  $p$  plays the exceptional role of the potential, the fields  $T, \mu_1, \dots, \mu_c$  appear as differentials while the conjugate densities  $\sigma, \rho_1, \dots, \rho_c$  appear as coefficients in the GD contact form. The choice of state variables is, however, largely arbitrary and variable transformations are frequently used in thermodynamic reasoning. For example, affine transformations in the field space have been extensively used recently in connection with critical points (Griffiths and Wheeler 1970) and phase transitions (Wheeler 1974)

<sup>†</sup> It is interesting to observe at this point that one could imagine the realisation of this possibility by a continuous variation of the molecular mass.



in multicomponent systems. Moreover, it may sometimes be convenient to change the role of the dependent (the potential) and independent fields, e.g. to interchange  $p$  and  $\mu$  in equation (2.16). This is a variable transformation which is considered appropriately in the extended field space introduced in § 1, but we will see below that a very interesting transformation of the density variables is associated with it. Finally, the introduction of a new potential to interchange the roles of fields and densities is commonly effected by the use of a Legendre transform.

The problem of determining all variable transformations which leave the fundamental equation of thermodynamics invariant is considered in this section. We will show that the various changes of variables mentioned above, which are in ordinary use in thermodynamics, are most conveniently interpreted in the  $(2c + 3)$ -dimensional contact space introduced in § 2. A general variable transformation in this space will have the equations

$$p' = p'(p, \mu_J, \rho_J) \quad \mu'_i = \mu'_i(p, \mu_J, \rho_J) \quad \rho'_i = \rho'_i(p, \mu_J, \rho_J). \quad (3.1)$$

In order that a transformation of this kind will preserve the contact structure of the space it is necessary that the equation

$$dp' - \rho'_i d\mu'_i = 0 \quad (3.2)$$

is satisfied whenever

$$dp - \rho_J d\mu_J = 0. \quad (3.3)$$

Equivalently, a transformation of the form (3.1) is called a *contact transformation* if the condition

$$dp' - \rho'_i d\mu'_i = \lambda(p, \mu_J, \rho_J)(dp - \rho_J d\mu_J) \quad (3.4)$$

is verified with  $\lambda \neq 0$ .

It can readily be shown that all transformations mentioned above may be considered as contact transformations of a particular type.

(a) Let us start our analysis from a general point transformation acting in the field space and therefore defined by equations of the form

$$\mu'_i = \mu'_i(\mu_0, \dots, \mu_c) \quad (i = 0, 1, \dots, c) \quad (3.5)$$

with

$$\partial(\mu'_0, \dots, \mu'_c) / \partial(\mu_0, \dots, \mu_c) \neq 0. \quad (3.6)$$

Then a contact transformation is obtained assuming that  $p$  behaves like a scalar, namely that  $p' = p$ . In this case we get from equation (3.4)  $\lambda = 1$  and

$$\rho_k = \rho'_i (\partial \mu'_i / \partial \mu_k) \quad (k = 0, 1, \dots, c) \quad (3.7)$$

from which the inverses are readily obtained by noting that

$$\frac{\partial \mu'_i}{\partial \mu_k} \frac{\partial \mu_k}{\partial \mu'_j} = \delta_{ij} \quad (3.8)$$

and therefore by multiplying both members of equation (3.7) by  $\partial \mu_k / \partial \mu'_j$  and summing over  $k$  we get

$$\rho'_j = \rho_k (\partial \mu_k / \partial \mu'_j). \quad (3.9)$$

The set of densities therefore behaves like a covariant vector and the new densities are expressed as linear functions of the old ones. We may summarise these results by writing down the equations of the corresponding contact transformations, namely,

$$p' = p \quad \mu'_i = \mu'_i(\mu_0, \dots, \mu_c) \quad \rho'_i = \rho_j(\partial\mu_j/\partial\mu'_i) \equiv \rho'_i(\mu_j, \rho_j). \quad (3.10)$$

It is of interest to calculate the functional determinant of this transformation:

$$\frac{\partial(p', \mu'_i, \rho'_i)}{\partial(p, \mu_j, \rho_j)} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \partial\mu'_i/\partial\mu_j & 0 \\ 0 & \partial\rho'_i/\partial\mu_j & \partial\mu_j/\partial\mu'_i \end{vmatrix} = 1. \quad (3.11)$$

One must observe that condition (3.6) implies that a transformation of this kind in which all the  $(c + 1)$  independent fields are involved is possible only in the neighbourhood of a single-phase solution. Indeed, condition (3.6) implies that all the fields may be varied independently, which is not the case, as a consequence of equations (2.13), on a coexistence locus. Appropriately restricted point transformations may obviously be used in the neighbourhood of a multiphase solution.

(b) We turn now to the consideration of an extended point transformation acting on the extended field space and therefore defined by equations of the form

$$p' = p'(p, \mu_j) \quad \mu'_i = \mu'_i(p, \mu_j). \quad (3.12)$$

Transformations of this kind occur when we change the field playing the exceptional role of the potential or on passing from the energy to the entropy scheme as described by equations (1.7) and (1.8). In all these cases equation (3.4) implies

$$\left(\frac{\partial p'}{\partial p} - \rho'_i \frac{\partial \mu'_i}{\partial p}\right) dp + \left(\frac{\partial p'}{\partial \mu_j} - \rho'_i \frac{\partial \mu'_i}{\partial \mu_j}\right) d\mu_j = \lambda (dp - \rho_j d\mu_j); \quad (3.13)$$

hence

$$\lambda = \frac{\partial p'}{\partial p} - \rho'_i \frac{\partial \mu'_i}{\partial p} \quad \lambda \rho_j = \rho'_i \frac{\partial \mu'_i}{\partial \mu_j} - \frac{\partial p'}{\partial \mu_j}. \quad (3.14)$$

The new densities together with  $\lambda$  may therefore be obtained by solving a system of linear equations. In particular, by eliminating  $\lambda$  we get

$$\rho_j = \frac{\rho'_i(\partial\mu'_i/\partial\mu_j) - (\partial p'/\partial\mu_j)}{(\partial p'/\partial p) - \rho'_i(\partial\mu'_i/\partial p)} \quad (3.15)$$

which defines locally a projective transformation. It is convenient to consider at this point the single-component system as an illustrative example.

We go back to the non-uniform notation and write the GD equation in the homogeneous form

$$-V dp + S dT + N d\mu = 0. \quad (3.16)$$

From this equation we may derive a fundamental equation in a number of ways, but two forms are commonly used, namely the one in which  $p$  plays the exceptional role of the potential

$$dp = \sigma dT + \rho d\mu \quad (3.17)$$

and the one in which such a role is played by  $\mu$ . Equations (3.12) become in this case

$$p' = \mu \quad T' = -T \quad \mu' = p \quad (3.18)$$

and therefore equations (3.14) give

$$\lambda = -\rho'_1 \quad \lambda\sigma = -\rho'_0 \quad \lambda\rho = -1, \tag{3.19}$$

from which we get

$$\lambda = -1/\rho \quad \rho'_0 = \sigma/\rho = s \quad \rho'_1 = 1/\rho = v. \tag{3.20}$$

The new fundamental equation will therefore take the form

$$d\mu = s dT' + v dp \tag{3.21}$$

while the functional determinant is readily evaluated to be

$$\frac{\partial(p'; T', \mu'; s, v)}{\partial(p; T, \mu; \sigma, \rho)} = -\frac{1}{\rho^3} = \lambda^3. \tag{3.22}$$

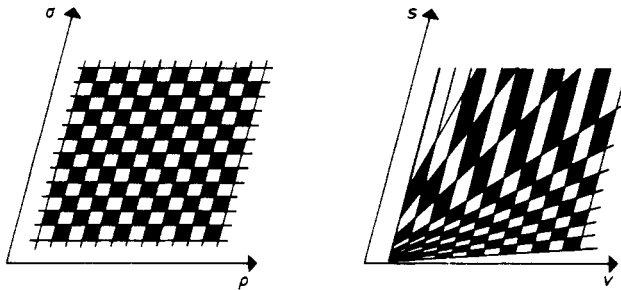
We interpret this transformation as follows. We may regard the extensive quantities  $S, V, N$  as a set of homogeneous coordinates in a two-dimensional density space. This interpretation is justified by the occurrence of the following two circumstances. First the triplet  $S = 0, V = 0, N = 0$  does not represent any thermodynamic state and, second, if  $\alpha$  is any positive real number the triplet  $(\alpha S, \alpha V, \alpha N)$  will represent the same state as the original one  $(S, V, N)$ . Now we may introduce in this projective density space a local coordinate system in a number of ways, but the most natural is to make use of the so called affine charts in which density variables are introduced as coordinates. By density, we mean here, in a somewhat broad sense, the ratio of any two extensive variables. In our example of a single-component system with a two-dimensional density space we may have three affine charts:

$$S: V: N \begin{cases} \sigma = S/V, & \rho = N/V & \text{if } V \neq 0 \\ s = S/N, & v = V/N & \text{if } N \neq 0 \\ x = V/S, & y = N/S & \text{if } S \neq 0. \end{cases} \tag{3.23}$$

From this point of view the variable transformation considered above appears as a transition from the first to the second of these charts, according to the equations

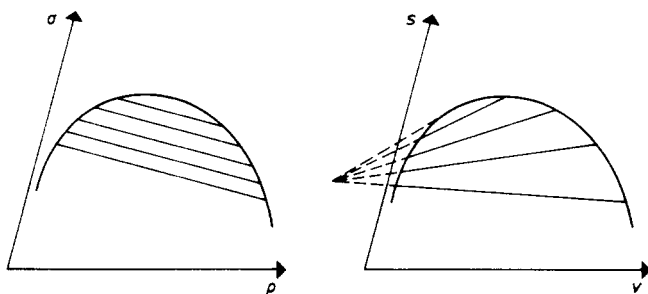
$$\left. \begin{matrix} v = \rho^{-1} \\ s = \sigma\rho^{-1} \end{matrix} \right\} \quad \left. \begin{matrix} \rho = v^{-1} \\ \sigma = sv^{-1} \end{matrix} \right\} \tag{3.24}$$

which represent a projective transformation in the density space. Its effect on a plane diagram is illustrated schematically in figure 1.



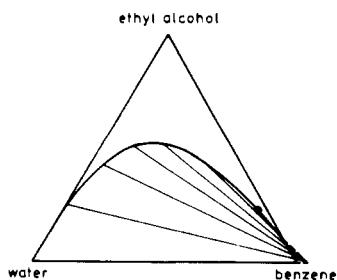
**Figure 1.** Schematic drawing illustrating the effect of the projective transformation given by equation (3.23).

Plane diagrams are frequently used to represent the thermodynamic properties of a system, but not too much attention has been given so far to the problem of distinguishing in such diagrams what are the intrinsic properties of the thermodynamic system and what are the artifacts of the description we give of the state space or of the operations, like sections, projections or both, which we make in order to get the diagram. The same thermodynamic object may be represented by quite different geometrical objects, from the point of view of a Euclidean mean, if different coordinate systems are used. Let us consider, for example, the effect of the transformation (3.24) on the coexistence curve of a simple fluid near its critical point. A number of observations indicate that  $T$  and  $\mu$  are a preferable choice of independent variables to  $T$  and  $p$  because of certain symmetries. We may argue that the effect of the transformation (3.23) on the coexistence curve is like that shown schematically in figure 2.



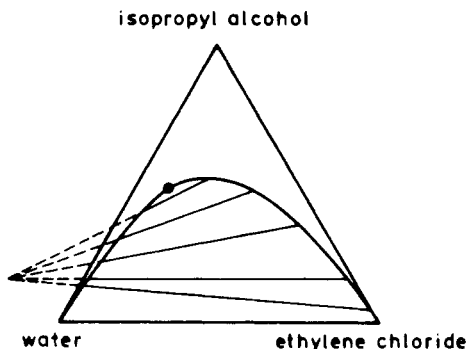
**Figure 2.** Qualitative picture illustrating the effect of the transformation given by equations (3.23) on the coexistence curve near the critical point of a simple fluid.

The orientation of tie lines in ternary systems at constant pressure and temperature is of particular interest to chemical engineers because it determines the selectivity of a solvent. Here affine charts are introduced through different kinds of concentration variables, often normalised so that the use of triangular diagrams is made convenient. Change of variables in order to make tie lines all parallel to the base line have often been considered. It has been found empirically (Francis 1963) for certain systems, like benzene–water–ethyl alcohol, that all the tie lines converge approximately toward a point on the extended base line, as illustrated in figure 3. It is then obviously possible, by means of a projective transformation of the type considered above for simple systems, to make all the tie lines horizontal. It is certainly more generally true that one



**Figure 3.** Coexistence curve illustrating the behaviour of tie lines of the ternary liquid system benzene–water–ethyl alcohol.

can find representations in which all the tie lines in an extended region near the plait converge towards a point not necessarily on the base line, as illustrated in figure 4 (Francis 1963). Admittedly a more careful discussion of this point should take into account the presence of critical singularities (Widom 1967), but we feel that the use of projective transformations may also be found enlightening for the interpretation of complex diagrams, although we have not investigated this point thus far.



**Figure 4.** Coexistence curve illustrating the behaviour of tie lines of the ternary liquid system water-isopropyl alcohol-ethylene chloride.

(c) Let us finally consider Legendre transformations. By means of these transformations we may change the role of fields and densities. The variable which has to be singled out to play the exceptional role of the potential is readily obtained as follows. Assume we want to change  $\mu_{q+1} \dots \mu_c$  by means of their respective conjugate densities  $\rho_{q+1} \dots \rho_c$ . We then observe that

$$d\left(p - \sum_{l=q+1}^c \rho_l \mu_l\right) = \sum_{i=0}^q \rho_i d\mu_i - \sum_{l=q+1}^c \mu_l d\rho_l \tag{3.25}$$

so that the new potential is clearly

$$p' = p - \sum_{l=q+1}^c \rho_l \mu_l \tag{3.26}$$

and the contact transformation will have the equations

$$p' = p - \sum_{l=1+1}^c \rho_l \mu_l \quad \mu'_i = \mu_i \quad \mu'_l = -\rho_l \quad \rho'_i = \rho_i \quad \rho'_l = \mu_l \tag{3.27}$$

( $i = 0, 1, \dots, q; l = q + 1, \dots, c$ ) with  $\lambda$  as well as the functional determinant equal to one. The new fundamental equation follows from (3.25) and (3.26) and is

$$dp' = \sum_{i=0}^q \rho_i d\mu_i - \sum_{l=q+1}^c \mu_l d\rho_l. \tag{3.28}$$

We can obtain the solutions of this new equation from those already obtained from the original GD equation and in this connection the relation between the contact transformation (3.27) and the usual Legendre transform will be established. Let us consider first a single-phase solution and let  $p = p(\mu_0, \dots, \mu_c)$  be the equation of its projection on the extended field space. For an equilibrium solution  $p$  is a convex function in all its

arguments and its Legendre transform with respect to the variables  $\mu_{q+1}, \dots, \mu_c$  is defined by

$$\phi(\mu_0 \dots \mu_q, \rho_{q+1} \dots \rho_c) = \min_{\{\mu_{q+1} \dots \mu_c\}} \left( p(\mu_0, \dots, \mu_c) - \sum_{l=q+1}^c \rho_l \mu_l \right). \quad (3.29)$$

Now

$$p' = \phi(\mu_0 \dots \mu_q, \rho_{q+1} \dots \rho_c) \quad (3.30)$$

clearly represents the equation of the projection on the extended field-density space, spanned by the variables  $p', \mu_0 \dots \mu_q, \rho_{q+1} \dots \rho_c$ , of the single-phase solution of equation (3.28). Indeed, from the definition (3.29) we have

$$\rho_l = \partial p / \partial \mu_l \quad (l = q + 1, \dots, c), \quad (3.31)$$

The introduction of densities as differentials in the fundamental equation is particularly meaningful to describe  $m$ -phase solutions. In this case the equation in the extended field-density space of the projection of a coexistence surface will be of the form

$$p' = p'(\mu_0 \dots \mu_{f-1}, \rho_f \dots \rho_c) = p(\mu_0 \dots \mu_{f-1}) - \sum_{J=f}^c \rho_J \mu_J(\mu_0, \dots, \mu_{f-1}). \quad (3.32)$$

Indeed,

$$\frac{\partial p'}{\partial \mu_i} = \frac{\partial p}{\partial \mu_i} - \sum_{J=f}^c \rho_J \frac{\partial \mu_J}{\partial \mu_i} = \rho_i \quad (i = 0, \dots, f - 1), \quad (3.33)$$

in agreement with (2.14).

We have therefore a  $(c + 1)$ -dimensional hypersurface irrespective of the number of phases, like the original surface in the contact space, which is linear in the density variables. It is a major merit of the contact group to respect the particular thermodynamic duality between fields and densities and, therefore, the notion of coexisting phases. The introduction of a density in place of a field or vice versa is possible only by means of a Legendre involution. A famous example provided by Gibbs (1876) may illustrate this point. Let the fundamental equation be written in the form

$$d\epsilon = T d\sigma + \sum_{i=1}^c \mu_i d\rho_i.$$

Then there is no contact transformation whose only effect is to interchange the role of  $\sigma$  and  $T$  while  $\epsilon$  still maintains the exceptional role of the potential. In other words, among all conceivable changes of thermodynamic variables, contact transformations are characterised as those which retain all the information contained in the fundamental equation. However, as in the case of canonical transformations in Hamiltonian mechanics, all the solutions, stable or not, are considered on the same footing.

### Acknowledgments

The author is grateful to one of the referees for his suggestions. In particular, the observation included as a footnote is due to him.

### Appendix. Contact manifolds (Arnold 1976)

Let  $M$  denote an  $N$ -dimensional differentiable manifold. In a small neighbourhood of any point of  $M$  a field of tangent hyperplanes (of dimensionality  $(N - 1)$ ) may be given by a linear differential form (also called one-form or Pfaffian form)

$$\omega = \sum_{k=1}^N a_k(x) dx_k \quad x \in M \quad (\text{A.1})$$

through the Pfaffian equation

$$\omega = 0. \quad (\text{A.2})$$

Therefore the field of hyperplanes defines a Pfaffian form apart from a non-zero factor.

Now we note that the number of terms appearing in a given Pfaffian form may depend on the coordinate system. For example, if  $f(x)$  is a given scalar function the differential of  $f$  is a Pfaffian form

$$df = \sum_{k=1}^N (\partial f / \partial x_k) dx_k \quad (\text{A.3})$$

with  $N$  terms. But if  $f(x)$  itself is assumed as one coordinate, say  $x_1$ , the differential will simply be written as

$$df \equiv dx_1 \quad (\text{A.4})$$

and contains one single term.

Obviously it is not always possible, given a Pfaffian form  $\omega$ , to find a coordinate system in which the form is written either as  $dx_1$  or  $x_2 dx_1$ . In these cases we say that the field of hyperplanes is integrable and  $x_2^{-1}$  is called an integrating factor. For a local study of the integrability of a given form  $\omega$  it is natural to consider the two-form  $d\omega$ , defined as the exterior derivative of  $\omega$ . If  $d\omega = 0$  then there exists a function  $f$  such that  $\omega = df$ , while if the Frobenius condition

$$\omega \times d\omega = 0 \quad (\text{A.5})$$

is verified then an integrating factor will exist. In three-space the Frobenius condition simply reduces to

$$a_1 \left( \frac{\partial a_2}{\partial x_3} - \frac{\partial a_3}{\partial x_2} \right) + a_2 \left( \frac{\partial a_3}{\partial x_1} - \frac{\partial a_1}{\partial x_3} \right) + a_3 \left( \frac{\partial a_1}{\partial x_2} - \frac{\partial a_2}{\partial x_1} \right) = 0. \quad (\text{A.6})$$

More generally the class  $c$  of a Pfaffian form, namely the smallest number of functions which represents the Pfaffian form, is related to the rank  $c'$  of the matrix  $d\omega$  by the equation

$$c = c' + \delta \quad (\text{A.7})$$

where  $\delta$  denotes either the number zero or unity. We have  $\delta = 0$  if the class is even and  $\delta = 1$  if it is odd. That the rank  $c'$  is always an even number follows from the antisymmetry of  $d\omega$ .

A field of hyperplanes is said to be non-degenerate if the rank  $c'$  of the two-form  $d\omega$  is identical with the dimensionality of the hyperplane  $\omega = 0$ . It follows from this definition that it is not possible to have a non-degenerate field of hyperplanes on a differentiable manifold of even dimensionality. Indeed, on such a manifold each

hyperplane is of odd dimensionality while the rank of  $d\omega$  must always be an even number. We are now in a position to define a contact manifold or contact space. A *contact manifold* is a differentiable manifold of odd dimensionality  $(2n + 1)$  endowed with a contact structure, i.e. a non-degenerate field of tangent hyperplanes of even dimensionality  $2n$ .

It can be shown (Darboux theorem) that one can always find a local coordinate system in which a contact structure is defined by a Pfaffian form written in canonical form

$$\omega = dz + x_k dy_k \tag{A.8}$$

where  $(x_1 \dots x_n), (y_1 \dots y_n)$  and  $z$  are the local coordinates. A contact transformation is a diffeomorphism of a contact manifold which preserves the contact structure, and it is therefore defined by equations of the type

$$z' = z'(z, y_J, x_J) \quad y'_i = y'_i(z, y_J, x_J) \quad x'_i = x'_i(z, y_J, x_J) \tag{A.9}$$

where the relation

$$dz' + x'_i dy'_i = \lambda(z, y_J, x_J)(dz + x_J dy_J) \tag{A.10}$$

must be satisfied with

$$\lambda(z, y_J, x_J) \neq 0. \tag{A.11}$$

We wish to show here that the functional determinant is given by

$$\frac{\partial(z', y'_i, x'_i)}{\partial(z, y_J, x_J)} = \lambda^{n+1}. \tag{A.12}$$

To this purpose we introduce a new variable  $V \neq 0$  and a new notation by setting

$$\begin{aligned} Y'_0 &\equiv z' & Y'_i &\equiv y'_i & Y_0 &\equiv z & Y_J &\equiv y_J \\ X'_0 &\equiv V/\lambda & X'_i &\equiv (V/\lambda)x'_i & X_0 &\equiv V & X_J &\equiv Vx_J. \end{aligned} \tag{A.13}$$

The relation (A.10), then, taking into account equation (A.11), assumes the form

$$X'_0 dY'_0 + X'_i dY'_i = X_0 dY_0 + X_J dY_J. \tag{A.14}$$

Now we note that we can express the  $2(n + 1)$  independent variables  $(z, y_J; V, x_J)$  in terms of the  $2(n + 1)$  variables  $(Y_0, Y_J; X_0, X_J)$  by solving equations (A.13):

$$z = Y_0 \quad y_J = Y_J \quad V = X_0 \quad x_J = X_J/V. \tag{A.15}$$

We can therefore calculate the quantities  $(Y'_0, Y'_i; X'_0, X'_i)$  as functions of  $(Y_0, Y_J; X_0, X_J)$ :

$$\begin{aligned} Y'_0 &= Y'_0(Y_0, Y_J; X_0, X_J) & X'_0 &= X'_0(Y_0, Y_J; X_0, X_J) \\ Y'_i &= Y'_i(Y_0, Y_J; X_0, X_J) & X'_i &= X'_i(Y_0, Y_J; X_0, X_J) \end{aligned} \tag{A.16}$$

and the relation (A.14) signifies that these represent a homogeneous canonical transformation. We have therefore

$$\partial(Y'_0, Y'_i, X'_0, X'_i)/\partial(Y_0, Y_J, X_0, X_J) = 1. \tag{A.17}$$



Then by simple operations we find

$$\frac{\partial(Y'_0, Y'_i, X'_0, X'_i)}{\partial(Y_0, Y_j, X_0, X_j)} = \frac{\partial(Y'_0, Y'_i, X'_i, X'_0)}{\partial(Y_0, Y_j, X_j, X_0)} = \frac{\partial(Y'_0, Y'_i, X'_i, X'_0)}{\partial(z, y_k, x_k, V)} \frac{\partial(z, y_k, x_k, V)}{\partial(Y_0, Y_j, X_j, X_0)}$$

On the other hand,

$$\frac{\partial(Y_0, Y_j, X_j, X_0)}{\partial(z, y_k, x_k, V)} = \frac{\partial(z, y_j, Vx_j, V)}{\partial(z, y_k, x_k, V)} = V^n$$

and therefore from (A.9)

$$\frac{\partial(Y'_0, Y'_i, X'_i, X'_0)}{\partial(z, y_k, x_k, V)} = V^n. \quad (\text{A.18})$$

Moreover

$$\begin{aligned} \frac{\partial(Y'_0, Y'_i, X'_i, X'_0)}{\partial(z, y_k, x_k, V)} &= \frac{\partial(z', y'_i, X'_0 x'_i, X'_0)}{\partial(z, y_k, x_k, V)} \\ &= \frac{\partial(z, y'_i, X'_0 x'_i, X'_0)}{\partial(z, y_k, x_k, X'_0)} \frac{\partial(z, y_k, x_k, X'_0)}{\partial(z, y_k, x_k, V)} \\ &= X_0'^n \frac{\partial X'_0}{\partial V} \frac{\partial(z', y'_i, x'_i)}{\partial(z, y_k, x_k)}. \end{aligned}$$

But taking into account that

$$\partial X'_0 / \partial V = 1/\lambda \quad \text{and} \quad X_0'^n = V^n / \lambda^n$$

and comparing with equation (A.18) we finally get equation (A.12).

*Note added in proof.* The orientation of the tie-lines in the  $(\rho, \sigma)$  plane in figure 2 is not drawn correctly. The entropy density of the liquid should be larger than that of the gas.

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