EXTREMUM PRINCIPLES IN THERMOSTATICS (*)

H. L. PINA

Centro de Termodinâmica Aplicada e Mecânica dos Fluidos
Instituto Superior Técnico, Lisboa

ABSTRACT — Thermostatics may be based on the following principle of equilibrium [1,5]:

Thermodynamic systems choose for equilibrium state that which minimizes the internal energy.

This minimum must be thought as subject to constraints, so the problem of finding the equilibrium state is one of minimization with constraints.

It is also said that this principle of minimum internal energy is equivalent to a principle of maximum entropy, the equivalence being shown by physical arguments. In this paper we present a rigorous demonstration of the equivalence of these two principles as well as the conditions for its validity, based on the theory of Lagrange multipliers.

1 — LAGRANGE MULTIPLIERS

Before going directly into Thermostatics we shall present the fundamental theorem of the theory of Lagrange multipliers [3, 4]. In what follows we assume all the functions to possess the required continuity and differentiability properties.

Theorem 1 Let $x \in \mathrm{R}^n$, $\mathrm{f}: \mathrm{R}^n \rightarrow \mathrm{R}$ and Ω the set defined by the constraints $g_\alpha: \mathrm{R}^n \rightarrow \mathrm{R}$

$$g_\alpha(x) = 0 \ , \ \alpha = 1, \ldots, m < n \qquad (1.1\ \mathrm{a})$$

(*) Results presented at the Conference of the Portuguese Physics Society (Lisbon, February 1978).

Suppose x_o affords a local minimum to $f(x)$ in Ω, and that x_o is normal, i.e., the matrix

$$\left(\frac{\partial g_\alpha}{\partial x^i} (x_o) \right) \quad (\alpha = 1, \ldots, m, \; i = 1, \ldots, n) \tag{1.1 b}$$

has rank m. Then there exist unique multipliers $\lambda_1, \ldots, \lambda_m$ such that the function

$$F(x) = f(x) + \sum_{\alpha=1}^{m} \lambda_\alpha \, g_\alpha (x) \tag{1.1 c}$$

is minimum at x_o, i.e.,

$$\nabla F(x_o) = \nabla f(x_o) + \sum_{\alpha=1}^{m} \lambda_\alpha \nabla g_\alpha (x_o) = 0 \tag{1.1 d}$$

Furthermore the inequality

$$F'' (x_o, h) \geqslant 0 \tag{1.1 e}$$

holds for all solutions $h \neq 0$ of the equations

$$g'_\alpha (x_o, h) = \langle \nabla g_\alpha (x_o), h \rangle = 0, \; \alpha = 1, \ldots, m \tag{1.1 f}$$

that is, for all h tangent to Ω.

(We are using the following notation:

$f'(x, h)$	denotes the differential of f at x in the direction of h
$\nabla f(x)$	is the gradient of f at x
$\langle . , . \rangle$	represents the inner product and
$\| \cdot \|$	is the associated norm).

The numbers $\lambda_1, \ldots, \lambda_\alpha$ are called Lagrange multipliers and the function $F(x)$ is known as the Lagrangean. The theorem presents only the necessary conditions for the existence of the multipliers. It is possible to show [3] that the condition

$$F'' (x_o, h) > 0 \tag{1.2}$$

for all solutions $h \neq 0$ of (1.1 f) is sufficient for the existence of a minimum.

We may now return to Thermostatics proper, which assumes that the state of perfect fluids [2,6] is determined by the values of the specific entropy s, the specific volume v and mole fractions $y_1, \ldots, y_r$ of the r chemical constituents of the fluid. The specific internal energy u is also a state function. When the states are homogeneous, the sole case treated in this paper, to minimize the global internal energy of a system is equivalent to minimize the specific internal energy at each of its points. Thus the equilibrium states are those which minimize

$$u = u\ (s, v, y_1, \ldots, y_r) \tag{1.3}$$

subject to appropriate constraints. Theorem 1 just presented yields a technique to obtain this minimum and therefore the states of equilibrium.

2 — PRINCIPLE OF RECIPROCITY

In this paragraph we show the following

Theorem 2. Let f, g, F, x_o and $\lambda_1, \ldots, \lambda_m$ be as in Theorem 1. Suppose that the $\lambda's$ are not all zero. Therefore there exists a $\lambda_\beta \neq 0$ such that x_o minimizes (if $\lambda_\beta > 0$) or maximizes (if $\lambda_\beta < 0$) $g_\beta(x)$ subject to the following set of constraints:

$$f(x) = f(x_o) \tag{2.1 a}$$

$$g_\alpha(x) = 0 \quad , \quad \alpha = 1, \ldots, \beta - 1,\ \beta + 1, \ldots, m \tag{2.1 b}$$

The proof is easy. According to Theorem 1, the point x_o minimizes the Lagrangean

$$\mathrm{F}\ (x) = f\ (x) + \sum_{\alpha=1}^{m} \lambda_\alpha\, g_\alpha(x) = \lambda_\beta\, g_\beta(x) + f(x) + \sum_{\alpha \neq \beta} \lambda_\alpha\, g_\alpha(x) \tag{2.2 a}$$

Since by hypothesis $\lambda_\beta \neq 0$ we may write

$$\frac{1}{\lambda_\beta}\ \mathrm{F}\ (x) = g_\beta(x) + \frac{1}{\lambda_\beta} f(x) + \sum_{\alpha \neq \beta} \frac{\lambda_\alpha}{\lambda_\beta}\, g_\alpha(x) \tag{2.2 b}$$

and because x_o yields a minimum to F (x), $\nabla \mathrm{F}(x_o) = 0$

Hence

$$0 = \frac{1}{\lambda_\beta} \nabla F(x_o) = \nabla g_\beta(x_o) + \frac{1}{\lambda_\beta} \nabla f(x_o) + \sum_{\alpha \neq \beta} \frac{\lambda_\alpha}{\lambda_\beta} \nabla g_\alpha(x_o) \quad (2.2\ c)$$

Put, for the sake of simplicity,

$$\bar{f}(x) = g_\beta(x) \quad (2.3\ a)$$

$$\bar{g}_\alpha(x) = g_\alpha(x) \text{ if } \alpha \neq \beta \quad (2.3\ b)$$

$$\bar{g}_\beta(x) = f(x) - f(x_o) \quad (2.3\ c)$$

and consequently

$$\bar{F}(x) = g_\beta(x) + \frac{1}{\lambda_\beta}[f(x) - f(x_o)] + \sum_{\alpha \neq \beta} \frac{\lambda_\alpha}{\lambda_\beta} g_\alpha(x) \quad (2.4\ c)$$

Expression (2.2 c) shows that $\bar{F}(x)$ is the Lagrangean and

$$\bar{\lambda}_\alpha = \frac{\lambda_\alpha}{\lambda_\beta} \text{ if } \alpha \neq \beta \quad (2.4\ d)$$

$$\bar{\lambda}_\beta = 1/\lambda_\beta \quad (2.4\ e)$$

the Lagrange multipliers of the extremization of $g_\beta(x)$ subject to constraints (2.1).

It remains to discuss the sign of the second differential $\bar{F}''(x_o, h)$. We must have now

$$\bar{F}''(x_o, h) = \frac{1}{\lambda_\beta} F''(x_o, h) \geqslant 0 \quad (2.5)$$

for all $h \neq 0$ which are solutions of the equations $f'(x_o, h) = 0$ and

$$g'_\alpha(x_o, h) = 0\ ,\ \alpha = 1, \ldots, \beta - 1, \beta + 1, \ldots, m \quad (2.6\ a,b)$$

We have to prove that the h's so obtained define the same set as in (1.1 f).

This can be done easily by noting that it x_o is a minimum of $f(x)$ subject to constraints (1.1 a) one must have

$$f'(x_o, h) = <\nabla f(x_o), h> = 0 \qquad (2.7\text{ a})$$

for all $h \neq 0$ satisfying (1.1 a) Similarly in the second case we have at x_o the equations

$$g'_\beta(x_o, h) = <\nabla g_\beta(x_o), h> = 0 \qquad (2.7\text{ b})$$

for all $h \neq 0$ satisfying (2.6 a, b). We see by inspection that the two sets of equations differ only in the order the equations are written and define thus the same h's. Therefore the sign of $\overline{F}''(x_o, h)$ is the same as $F''(x_o, h)$ if $\lambda\beta > 0$ and the contrary if $\lambda\beta < 0$, which completes the proof.

We are in condition to apply the reciprocity principle to Thermostatics. Consider the following problem: minimize

$$u = u(s, v, y_1, \dots, y_r) \qquad (2.8\text{ a})$$

subject to

$$s = s_o \qquad (2.8\text{ b})$$

and eventually to other constraints which we omit now. According to theorem 1 we must have that at equilibrium (which we denote by the subscript o)

$$\frac{\partial u}{\partial s}(s_o, v_o, y_{1o}, \dots, y_{ro}) + \lambda = 0 \qquad (2.9)$$

and recalling the definition of absolute temperature T

$$T \equiv \frac{\partial u}{\partial s}(s, v, y_1, \dots y_r) \qquad (2.10)$$

we see that the minimum of internal energy is equivalent to the maximum of entropy if and only if

$$-\lambda = T > 0 \qquad (2.11)$$

The reciprocity principle in this case collapses at $T = 0$. For systems with a negative temperature the minimum principle of internal energy is associated with a minimum principle of entropy, and a maximum principle of entropy with a maximum principle of internal energy.

3 — INEQUALITY CONSTRAINTS

In the preceding paragraph we have concentrated on the variables u and s to derive the reciprocity principle. When we observe other variables as v and y_i's we recognize that they are by definition non-negative. Thus we must take this fact in due account when setting the minimization or maximization problem. If constraints are given by inequalities the theorem of Kuhn-Tucker applies [3, 4]. Before presenting this theorem some preliminary definitions are required.

Definition 3.1 Let the inequality constraints

$$g_\alpha(x) \leqslant 0 \quad , \quad \alpha = 1, \ldots, m \tag{3.1}$$

be given. If $g_\beta(x_o) = 0$ the βth constraint is said to be *active* at x_o. If $g_\beta(x_o) < 0$ the βth constraint is said to be *inactive* at x_o.

Definition 3.2 Let Ω be the set of points x satisfying

$$g_\alpha(x) \leqslant 0 \, , \, \alpha = 1, \ldots, p \, ; \, g_\beta(x) = 0 \, , \, \beta = p+1, \ldots, m \qquad (3.2 \text{ a, b})$$

A point x_o is *regular* if every outer normal w of Ω at x_o is expressible in the form

$$w = \sum_{\alpha=1}^{m} \lambda_\alpha \nabla g_\alpha(x_o) \qquad (3.2 \text{ c})$$

where $\lambda_1, \ldots, \lambda_p$ are non-negative and $\lambda_\alpha = 0$ wherever $g_\alpha(x_o) < 0$, *i.e.*, the αth constraint is inactive.

We are in condition to give the following

Theorem 3. Suppose x_o yields a local minimum to $f(x)$ on the set Ω defined by the constraints

$$g_{\alpha}(x) \leqslant 0 \ , \ \alpha = 1, \ldots, p \ ; \ g_{\beta}(x) = 0 \ , \ \beta = p+1, \ldots, m \qquad (3.3\ a)$$

If x_o is a regular point of Ω then there exist multipliers $\lambda_1, \ldots, \lambda_m$ such that

$$\lambda_{\alpha} \geqslant 0 \ , \ \alpha = 1, \ldots, p \text{ with } \lambda_{\alpha} = 0 \text{ if } g_{\alpha}(x_o) < 0 \qquad (3.3\ b)$$

and such that the function

$$\mathrm{F}(x) = f(x) + \sum_{\alpha=1}^{m} \lambda_{\alpha} g_{\alpha}(x) \qquad (3.3\ c)$$

is a minimum at x_o, i.e.,

$$\nabla \mathrm{F}(x_o) = 0 \qquad (3.3\ d)$$

and

$$\mathrm{F}''(x_o, h) > 0 \qquad (3.3\ e)$$

for all $h \neq 0$ satisfying the relations:

$$g'_{\alpha}(x_o, h) \leqslant 0 \text{ if } \alpha \text{ is active and } \lambda_{\alpha} = 0 \qquad (3.3\ f)$$

$$g'_{\alpha}(x_o, h) = 0 \text{ if } \alpha \text{ is active and } \lambda_{\alpha} > 0 \qquad (3.3\ g)$$

$$g'_{\alpha}(x_o, h) = 0 \text{ if } \alpha \text{ is inactive} \qquad (3.3\ h)$$

We are now in position to solve the following problem: minimize $u = u(s, v, y_1, \ldots, y_r)$ subject to the constraints:

$$s - s_o = 0 \qquad (3.4\ a)$$

$$-v \leqslant 0 \qquad (3.4\ b)$$

$$v - b \leqslant 0 \qquad (3.4\ c)$$

$$-y_i \leqslant 0 \ , \ i = 1, \ldots, r \qquad (3.4\ d)$$

$$\sum_{i=1}^{r} y_i - 1 = 0 \qquad (3.4\ e)$$

Constraint (3.4 a) specifies the value of the entropy and constraint (3.4 b) assures us that the solution of the above problem will not yield negative values for the volume. Constraint (3.4 c) is introduced here because for perfect fluids the volume is not specified in advance but only an upper bound is given. For instance, when dealing with gases, the volume of the container is such an upper bound, but there is no a priori reason to suppose the gas will never assume a volume less than this. If in fact we do require that the gas occupies always the largest volume available to it then we must be aware we have introduced a constitutive assumption. Constraints (3.4 d, e) are mere consequences of the definitions of molar fractions.

Applying theorem 3 we obtain

$$\partial u / \partial s \ (\ldots) + \lambda_1 = 0 \tag{3.5 a}$$

$$\partial u / \partial v \ (\ldots) - \lambda_2 = 0 , \lambda_2 > 0 , \lambda_2 = 0 \text{ if } v > 0 \tag{3.5 b}$$

$$\partial u / \partial v \ (\ldots) + \lambda_3 = 0 , \lambda_3 > 0 , \lambda_3 = 0 \text{ if } v < b \tag{3.5 c}$$

$$\partial u / \partial y_i \ (\ldots) - \lambda_{3+i} = 0 , \lambda_{3+i} > 0 , \lambda_{3+i} = 0 \text{ if } y_i > 0 \tag{3.5 d}$$

$$\partial u / \partial y_i \ (\ldots) - \lambda_{3+r+i} = 0 \tag{3.5 e}$$

where the symbol (...) stands as an abbreviation to the list of variables $(s_o, v_o, y_{1o}, \ldots, y_{ro})$.

As we have seen, the temperature is assumed to be non-negative, therefore by (2.11) $-\lambda_1 = T \geqslant 0$. This implies that the entropy at the minimum is s_o. There is no loss of generality in this case to substitute the equality constraint (3.4 a) by an inequality constraint

$$s - s_o < 0 \tag{3.6}$$

The pressure is given in Thermostatics by

$$P = -\frac{\partial u}{\partial v}(s, v, y_1, \ldots, y_r) \tag{3.7}$$

If a perfect fluid is such that the constraint (3.5 c) is always active for all $b \geqslant 0$ then we can assert by (3.4 c) that the pressure P is a non-negative function or that the internal energy u is a non-increasing function of the volume v. It is easily seen that the converse is also true.

If we had set $v = b$ instead of (3.4 c), the conclusion we have just reached would not have been possible. In fact we would have introduced, in an implicit way, a constitutive hypothesis.

4 — LAGRANGEANS IN THERMOSTATICS

Let us return to the problem of minimising $u\ (s, v, y_1, \ldots, y_r)$ subject to $s - s_o \leqslant 0$. As we have shown in 3, the Lagrangean function for this case is

$$f = u\ (s, v, y_1, \ldots\ y_r) - T_o\ (s - s_o) \qquad (4.1\ a)$$

We can write also that, because f is minimum at equilibrium,

$$u\ (s_o, v_o, y_{1o}, \ldots, y_{ro}) \leqslant u\ (s, v, y_1, \ldots, y_r) - T_o\ (s - s_o) \quad (4.1\ b)$$

or

$$u\ (s_o, v_o, y_{1o}, \ldots, y_{ro}) - T_o\ s_o \leqslant u\ (s, v, y_1, \ldots, y_r) - T_o\ s \quad (4.2)$$

We recognize both members of this inequality to be the Helmholtz free energy at the temperature T_o, evaluated at equilibrium (the LHS) and at any state (the RHS). Therefore for a given temperatura T_o the equilibrium state minimizes the Helmholtz free energy.

It is now immediate that the corresponding principle for the constraint $v - v_o \leqslant 0$ is the minimization of the entalpy $h = u + Pv$, such that

$$u\ (s_o, v_o, y_{1o}, \ldots, y_{ro}) + P_o\, v_o \leqslant u\ (s, v, y_1, \ldots, y_r) + P_o\, v \quad (4.3)$$

For the set of constraints $s - s_o \leqslant 0$, $v - v_o \leqslant 0$ the Gibbs free energy $g = u - Ts + Pv$ is the one to minimize and we have

$$u\ (s_o, v_o, y_{ko}) + P_o\ v_o - T_o\ s_o \leqslant u\ (s, v, y_k) + P_o\, v - T_o\, s \quad (4.4)$$

This inequality is identical to that postulated by Coleman and Noll [2].

The author wishes to thank Professor A. G. Portela for several fruitful discussions on the subject of this paper.

REFERENCES

[1] A. B. CALLEN, *Thermodynamics,* Wiley, 1960.

[2] B. D. COLEMAN and W. NOLL, *Arch. Rat. Mech. Anal.,* **4**, 2, 1959.

[3] M. R. HESTENES, *Optimization Theory,* Wiley, 1975.

[4] D. G. LUENBERGER, *Optimization by Vector Space Methods,* Wiley, 1969.

[5] L. TISZA, *Generalized Thermodyamics,* MIT Press, 1966.

[6] C. TRUESDELL and W. NOLL, *The Non-Linear Field Theories of Mechanics,* Encyclopedia of Physics, Vol. III/3, Springer, 1965.