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ABOUT THE ROLE OF CONSTRAINTS IN THE LINEAR RELAXATIONAL BEHAVIOUR OF THERMODYNAMIC SYSTEMS

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A formalism is presented by which the linear relaxational behaviour of thermodynamic systems can be described. Instead of using the concept of internal variables of state a set of so-called constraint equations is introduced. These equations represent structural properties of the system and turn out to be related to the shape of the relaxation and retardation spectra of the system. Furthermore some problems concerning the concept of internal variables of state are clarified.

1. Introduction

Since the pioneering work of Meixner[1]) and also that of Biot[2]) it is well known that in a thermodynamic description of relaxation phenomena it is useful to introduce a set of so-called "internal variables of state". In this approach one assumes that the thermodynamic state of a system is fully determined by a complete set of external and internal variables of state. The basic results are obtained then from an expansion of the internal energy or any other thermodynamic potential in these variables and by introducing linear rate equations. This approach has proved to be successful in several branches of physics. For the case of the mechanical behaviour of materials for instance one could mention the work of Schapery[3]), Valanis[4]), Kestin and Rice[5]), Kluitenberg[6]), Lubliner[7]) and Sidoroff[8]).

Although the theory has already been extended into several directions, for instance by including transport phenomena , thermal effects and non-linear behaviour, some fundamental problems concerning the concept of internal variables of state seem to be still unclarified. A basic problem is how to discriminate in the Gibbs fundamental equation between external and internal variables. About this point still some confusion seems to exist; for a recent discussion we refer to refs. 9 and 10.

In the present paper an approach is given in which no distinguishment between internal and external variables is made. Instead a set of so-called constraint equations is introduced. These equations represent structural properties of the system and turn out to be related in a simple way to the shape of its relaxation and retardation spectra.

In order to concentrate on the essential parts of the subject only homogeneous systems in which no transport phenomena take place are considered. For the same reason temperature effects are left out of consideration as well.

2. Basic thermodynamic relations

We consider a system for which a finite set of variables q_i^t $(i = 1, 2, \ldots, k)$ exists, such that the internal energy can be expressed as

$$u = u(s, q_1^t, \ldots, q_k^t), \tag{2.1}$$

where s is the entropy. This relation is called the Gibbs fundamental equation of the system; it contains all information about its thermodynamic properties. The variables q_i^t are called: thermodynamic variables of state.

In differential form (2.1) reads:

$$\mathrm{d}u = T\,\mathrm{d}s + \sum_{i=1}^{k} p_i^t\,\mathrm{d}q_i^t, \tag{2.2}$$

where

$$T \equiv \frac{\partial u(s, q_1^t, \ldots, q_k^t)}{\partial s} = T(s, q_1^t, \ldots, q_k^t) \tag{2.3}$$

is the temperature and

$$p_i^t \equiv \frac{\partial u(s, q_1^t, \ldots, q_k^t)}{\partial q_i^t} = p_i^t(s, q_1^t, \ldots, q_k^t). \tag{2.4}$$

In this paper only isothermal processes will be considered. In that case from (2.3) we obtain: $s = s(q_1^t, \ldots, q_k^t)$ and (2.4) becomes:

$$p_i^t = p_i^t(q_1^t, \ldots, q_k^t), \quad (i = 1, 2, \ldots, k). \tag{2.5}$$

These relations are the thermodynamic equations of state of the system.

The change of internal energy is, besides by (2.2), also given by a balance equation which in particular cases can be derived from the energy-conservation principle with the aid of the expression of kinetic energy and field energies (see for instance ref. 11, chapters II and XIV). This equation takes the form

$$\mathrm{d}u = \mathrm{d}Q + \mathrm{d}W, \tag{2.6}$$

where dQ is the heat supplied to the system and dW, which has the form

$$dW = \sum_{j=1}^{l} p_j^e \, dq_j^e, \tag{2.7}$$

is the part of the work supplied to the system which does not contribute to the kinetic and field energies of the system.

The quantities p_j^e and dq_j^e will be called external forces and displacements, respectively. It is important to note that these quantities will in general not coincide with the thermodynamic forces p_i^t and the increments of the thermodynamic variables of state dq_i^t. Even the numbers k and l in (2.2) and (2.7) are in general not the same. For a detailed discussion about this point we refer to ref. 12.

The change of entropy can be split up into two parts:

$$dS = d_eS + d_iS. \tag{2.8}$$

Here d_eS is the part of the entropy change due to the interactions of the system with its surroundings and d_iS the entropy change due to irreversible processes in the system. These quantities are called the entropy supply and the entropy production, respectively. Since, as has been stated already in the Introduction, we only consider homogeneous systems in a uniform state, the entropy supply takes the simple form

$$d_eS = \frac{dQ}{T}. \tag{2.9}$$

From (2.2), (2.6), (2.7) and (2.9) we obtain:

$$T \, d_iS = -\sum_{i=1}^{k} p_i^t \, dq_i^t + \sum_{j=1}^{l} p_j^e \, dq_j^e. \tag{2.10}$$

This quantity, being the difference between the work externally supplied to the system and the work reversibly stored in the system, will be called the dissipation.

Although there is a fundamental difference between the forces and displacements in the two work terms in (2.10), certain relations between these may exist in general. We first give some examples of such relations.

In the simplest example of a system with internal variables of state (ref. 1) one has:

$$p_j^t = p_j^e \qquad (j = 1, 2, \ldots, l; l < k), \tag{2.11}$$

$$dq_j^t = dq_j^e \qquad (j = 1, 2, \ldots, l; l < k). \tag{2.12}$$

The quantities q_j^t $(j = 1, 2, \ldots, l)$ then are the external and the remaining ones q_j^t $(j = l+1, l+2, \ldots, k)$ the internal variables of state. The forces p_i^t $(i = l +$

1, $l+2, \ldots, k$) conjugate to the internal variables of state are minus the so-called affinities.

Sometimes[2]) the only relations between the t and e variables assumed to exist are the equations (2.12). In that case the differences $p_j^e - p_j^t$ $(j = 1, \ldots, l)$ occur as forces in the expression of the entropy production. In mechanical systems such forces have the significance of viscous stresses.

A third example of relations between variables in the Gibbs relation and the internal energy balance can be found in Kluitenberg's theory[6]) of the visco-elastic behaviour of materials. In this theory relations of the form

$$\mathrm{d}q_1^e = \sum_{i=1}^{k} \mathrm{d}q_i^t \tag{2.13}$$

are considered. The variables q_i^t are called[6]) partial strains.

By the equations (2.11)–(2.13) certain structural properties are assigned to the system: the way by which the parts of the system in which a reversible storage of energy is possible (t variables) are connected with the environment (e variables) is specified. Such equations, the nature of which is essentially different from that of the thermodynamic equations of state, will be called constraint equations. A general discussion of the properties of linear constraint equations will be given in the next section.

3. Constraint equations

In this section some general properties of linear constraint equations will be discussed. In order to facilitate this discussion we will use some concepts of linear algebra. The quantities p_i^t will be considered as the components of a vector p^t in a k-dimensional linear space P^t:

$$p^t \in \mathsf{P}^t, \quad \dim \mathsf{P}^t = k \tag{3.1}$$

and similarly $\mathrm{d}q_i^t$ as the components of a vector $\mathrm{d}q^t$ in a k-dimensional linear space Q^t:

$$\mathrm{d}q^t \in \mathsf{Q}^t, \quad \dim \mathsf{Q}^t = k. \tag{3.2}$$

By defining a scalar product between the spaces P^t and Q^t by

$$p^t\,\mathrm{d}q^t = \sum_{i=1}^{k} p_i^t\,\mathrm{d}q_i^t \tag{3.3}$$

these spaces become dual to each other (see for instance ref. 13).

Similarly to (3.1) and (3.2) vectors p^e and $\mathrm{d}q^e$ and spaces P^e and Q^e are defined such that

$$p^e \in \mathsf{P}^e, \quad \dim \mathsf{P}^e = l, \tag{3.4}$$

$$dq^e \in \mathsf{Q}^e, \quad \dim \mathsf{Q}^e = l, \tag{3.5}$$

and finally spaces P^0 and Q^0 are defined as the external direct sums[13])

$$\mathsf{P}^0 = \mathsf{P}^t \oplus \mathsf{P}^e, \quad \dim \mathsf{P}^0 = k + l, \tag{3.6}$$

$$\mathsf{Q}^0 = \mathsf{Q}^t \oplus \mathsf{Q}^e, \quad \dim \mathsf{Q}^0 = k + l. \tag{3.7}$$

In the latter spaces we define vectors p^0 and dq^0 as

$$p^0 = -p^t + p^e, \tag{3.8}$$

$$dq^0 = dq^t + dq^e. \tag{3.9}$$

Here and elsewhere in this paper no notational distinction will be made between a vector, say p^t considered as an element of P^t or as an element of $\mathsf{P}^t \oplus \mathsf{P}^e$, although in the latter case the notation $(p^t, 0)$ would be formally more correct.

By introducing a scalar product defined by (3.8), (3.9) and

$$p^0\, dq^0 = -p^t\, dq^t + p^e\, dq^e \tag{3.10}$$

the spaces P^0 and Q^0 become dual to each other. Linear constraint equations between force variables and between displacement variables will be represented by the equations

$$\mathsf{C}^0 p^0 = 0 \tag{3.11}$$

and

$$\mathsf{D}^0\, dq^0 = 0 \tag{3.12}$$

respectively, where C^0: $\mathsf{P}^0 \to \mathsf{P}^0$ and D^0: $\mathsf{Q}^0 \to \mathsf{Q}^0$ are linear mappings. Since, for instance, an equation $\tilde{\mathsf{C}}^0 \rho^0 = 0$, where $\tilde{\mathsf{C}}^0 p^0 = 0$, and $\Lambda : \mathsf{P}^0 \to \mathsf{P}^0$ is a regular mapping, is equivalent to (3.11) the mappings C^0 and D^0 are not uniquely determined. An important property, however, which remains invariant under the transformations just mentioned is their rank. The ranks of the mappings C^0 and D^0 are denoted by

$$r(\mathsf{C}^0) = g, \tag{3.13}$$

$$r(\mathsf{D}^0) = h. \tag{3.14}$$

Physically this means that there are g independent relations between the thermodynamic and the external forces and h independent relations between the thermodynamic and the external displacements.

The number of constraints on the force variables cannot exceed the number of external variables, since otherwise the constraint equation (3.11) would imply relations between thermodynamic variables; this would be in contradiction with the assumed independency of those variables. Similar statements can be deduced from the mutual independency of the external variables and of the mutual independency of the displacement variables. So we have:

$$g \leqslant k, \quad g \leqslant l, \quad h \leqslant k, \quad h \leqslant l. \tag{3.15}$$

From (3.11) and (3.12) it follows that the vectors $\mathrm{d}q^0$ are restricted to certain subspaces of P^0 and Q^0, respectively, say

$$p^0 \in \mathsf{R}^0 \subset \mathsf{P}^0, \tag{3.16}$$

$$\mathrm{d}q^0 \in \mathsf{S}^0 \subset \mathsf{Q}^0. \tag{3.17}$$

The spaces R^0 and S^0 are the kernels of the operators C^0 and D^0, respectively:

$$\mathsf{R}^0 = \ker \mathsf{C}^0, \tag{3.18}$$

$$\mathsf{S}^0 = \ker \mathsf{D}^0. \tag{3.19}$$

From (3.1), (3.2), (3.13) and (3.14) their dimensions are calculated to be

$$\dim \mathsf{R}^0 = \dim \mathsf{P}^0 - r(\mathsf{C}^0) = k + l - g, \tag{3.20}$$

$$\dim \mathsf{S}^0 = \dim \mathsf{Q}^0 - r(\mathsf{D}^0) = k + l - h. \tag{3.21}$$

The expression (2.10) for the dissipation can, with the aid of (3.10), be written as

$$T\, \mathrm{d_i}S = p^0\, \mathrm{d}q^0. \tag{3.22}$$

For $p^0 \in \mathsf{R}^0$ and $\mathrm{d}q^0 \in \mathsf{S}^0$ this bilinear form will in general be degenerate. This means that for instance non-zero vectors $p^0 \in \mathsf{R}^0$ may exist for which $p^0\, \mathrm{d}q^0 = 0$ for all $\mathrm{d}q^0 \in \mathsf{S}^0$. Therefore the bilinear form (3.22) does not define a scalar product between the spaces R^0 and S^0.

It is possible, however, to introduce vectors p^d and $\mathrm{d}q^\mathrm{d}$ and spaces P^d and Q^d, such that

$$T\, \mathrm{d_i}S = p^\mathrm{d}\, \mathrm{d}q^\mathrm{d}, \tag{3.23}$$

$$p^\mathrm{d} \in \mathsf{P}^\mathrm{d} \subset \mathsf{R}^0, \tag{3.24}$$

$$\mathrm{d}q^\mathrm{d} \in \mathsf{Q}^\mathrm{d} \subset \mathsf{S}^0, \tag{3.25}$$

where $p^\mathrm{d}\, \mathrm{d}q^\mathrm{d}$ is a non-degenerate bilinear form. In order to proof this we note that the orthogonal complements $\mathsf{R}^{0\perp}$ and $\mathsf{S}^{0\perp}$ of R^0 and S^0 in Q^0 and P^0, respectively, have the property that

$$\mathsf{R}^{0\perp} \subset \mathsf{S}^0; \ \ \mathsf{S}^{0\perp} \subset \mathsf{R}^0. \tag{3.26}$$

These relations, which are not just mathematical identities but relations rooted in thermodynamics, can be derived as follows. The existence of a Gibbs fundamental equation (2.1) implies that in certain subsystems of the system – which will be called "reversible elements" in the present discussion – a reversible exchange of energy takes place. Therefore, by connecting these reversible elements directly to the external sources, represented by the vectors p^e and dq^e, it should be possible – in principle – to alter the system in such a way that only reversible processes can take place in it.

In the present formalism the coupling of the reversible elements of the external sources means that new constraints are added to the existing ones. The spaces R^0 and S^0 are transformed then into new ones, say $\tilde{\mathsf{R}}^0$ and $\tilde{\mathsf{S}}^0$, which will be subspaces of the former:

$$\tilde{\mathsf{R}}^0 \subset \mathsf{R}^0, \quad \tilde{\mathsf{S}}^0 \subset \mathsf{S}^0, \tag{3.27}$$

while the numbers g and h, defined in (3.13) and (3.14), are changed into $\tilde{g} \geqslant g$ and $\tilde{h} \geqslant h$.

In the altered system as a result of the added constraints a mutual dependency among the force or displacement variables may exist. The inequalities (3.15) do not have to apply therefore in this case. Since, however, the final set of constraint equations still has to be compatible with the (k) thermodynamic equations of state (2.5) and since in each of the (l) sources just one variable is independent (either a force variable or a displacement variable), the total number of constraint equations may not exceed the total number $(k + l)$ of reversible elements and sources; so we have:

$$\tilde{g} + \tilde{h} \leqslant k + l. \tag{3.28}$$

In the altered system all processes which are compatible with the constraints are reversible; this implies:

$$p^0\, dq^0 = 0, \quad \forall p^0 \in \tilde{\mathsf{R}}^0, \quad dq^0 \in \tilde{\mathsf{S}}^0. \tag{3.29}$$

So we have:

$$\tilde{\mathsf{R}}^0 \subset \tilde{\mathsf{S}}^{0\perp} \tag{3.30}$$

(which implies that also $\tilde{\mathsf{S}}^0 \subset \tilde{\mathsf{R}}^{0\perp}$).

Since by (3.20) $\dim \tilde{\mathsf{R}}^0 = k + l - \tilde{g}$ and by (3.7) and (3.21) $\dim \tilde{\mathsf{S}}^{0\perp} = \dim \mathsf{Q}^0 - \dim \tilde{\mathsf{S}}^0 = \tilde{h}$, (3.30) implies that

$$\tilde{g} + \tilde{h} \geqslant k + l, \tag{3.31}$$

which is consistent with (3.28) only if the equality sign applies. So

$$\tilde{\mathsf{R}}^0 = \tilde{\mathsf{S}}^{0\perp}. \tag{3.32}$$

From (3.27) we obtain:

$$\mathsf{R}^{0\perp} \subset \tilde{\mathsf{R}}^{0\perp}. \tag{3.33}$$

so by (3.32) and (3.27):

$$\mathsf{R}^{0\perp} \subset \tilde{\mathsf{R}}^{0\perp} = \tilde{\mathsf{S}}^{0} \subset \mathsf{S}^{0}, \tag{3.34}$$

which completes the proof of the first relation (3.26). The second relation (3.26) can be proved in a similar way. The spaces P^{d} and Q^{d} of (3.24) and (3.25) can be defined now as complementary subspaces of $\mathsf{S}^{0\perp}$ and $\mathsf{R}^{0\perp}$ in respectively R^0 and S^0, which may be chosen arbitrarily. The spaces R^0 and S^0 can be considered then as the direct sums

$$\mathsf{R}^0 = \mathsf{S}^{0\perp} \oplus \mathsf{P}^{\mathrm{d}}, \tag{3.35}$$

$$\mathsf{S}^0 = \mathsf{R}^{0\perp} \oplus \mathsf{Q}^{\mathrm{d}}. \tag{3.36}$$

This makes it possible to define vectors $p^{\mathrm{r}} \in \mathsf{S}^{0\perp}$, $p^{\mathrm{d}} \in \mathsf{P}^{\mathrm{d}}$, $\mathrm{d}q^{\mathrm{r}} \in \mathsf{R}^{0\perp}$ and $\mathrm{d}q^{\mathrm{d}} \in \mathsf{Q}^{\mathrm{d}}$, such that for each $p^0 \in \mathsf{R}^0$ and $\mathrm{d}q^0 \in \mathsf{S}^0$

$$p^0 = p^{\mathrm{r}} + p^{\mathrm{d}} \tag{3.37}$$

and

$$\mathrm{d}q^0 = \mathrm{d}q^{\mathrm{r}} + \mathrm{d}q^{\mathrm{d}}. \tag{3.38}$$

Substitution of these in the expression (3.22) of the dissipation gives

$$T\,\mathrm{d_i}S = p^0\,\mathrm{d}q^0 = (p^{\mathrm{r}} + p^{\mathrm{d}})(\mathrm{d}q^{\mathrm{r}} + \mathrm{d}q^{\mathrm{d}}) = p^{\mathrm{d}}\,\mathrm{d}q^{\mathrm{d}}, \tag{3.39}$$

which is a non-degenerate bilinear form on R^0 and S^0. Thus the desired form (3.23) is obtained.

The dimensions of the spaces $\mathsf{R}^{0\perp}$ and $\mathsf{S}^{0\perp}$ are (see the statements below eq. (3.30)):

$$\dim \mathsf{R}^{0\perp} = g, \tag{3.40}$$

$$\dim S^{0\perp} = h. \tag{3.41}$$

So by (3.20), (3.21), (3.35) and (3.36) we have:

$$\dim \mathsf{P}^{\mathrm{d}} = \dim \mathsf{Q}^{\mathrm{d}} = m, \tag{3.42}$$

where

$$m \equiv k + l - g - h. \tag{3.43}$$

Physically m denotes the number of independent 'forces' and 'fluxes' in the bilinear form of the entropy production.

For the further discussion it is convenient to define spaces P and Q as

$$\mathsf{P} = \mathsf{P}^0 \oplus \mathsf{P}^d, \quad \dim \mathsf{P} = k + l + m, \tag{3.44}$$

$$\mathsf{Q} = \mathsf{Q}^0 \oplus \mathsf{Q}^d, \quad \dim \mathsf{Q} = k + l + m. \tag{3.45}$$

In these spaces we define vector $p \in \mathsf{P}$ and $dq \in \mathsf{Q}$ as

$$p = p^0 - p^d = -p^t + p^e - p^d, \tag{3.46}$$

$$dq = dq^0 + dq^d = dq^t + dq^e + dq^d. \tag{3.47}$$

The constraint equations (3.11) and (3.12) lead to similar equations in the spaces P and Q, say

$$Cp = 0, \tag{3.48}$$

$$D\, dq = 0. \tag{3.49}$$

Analogously to (3.18) and (3.19) we define spaces R and S as

$$\mathsf{R} = \ker C, \tag{3.50}$$

$$\mathsf{S} = \ker D. \tag{3.51}$$

So the constraints can be stated as

$$p \in \mathsf{R} \subset \mathsf{P}, \tag{3.52}$$

$$dq \in \mathsf{S} \subset \mathsf{Q}, \tag{3.53}$$

which means that the vectors p and dq are restricted to certain subspaces R and S of P and Q, respectively. We define a scalar product between the spaces P and Q by

$$p\, dq = p^0\, dq^0 - p^d\, dq^d. \tag{3.54}$$

From (3.22) and (3.23) we then have:

$$p\, dq = 0 \tag{3.55}$$

for all $p \in \mathsf{R}$ and $dq \in \mathsf{S}$. This means that the spaces R and S are orthogonal with respect to the scalar product defined by (3.54); that is

$$\mathsf{R} \subset \mathsf{S}^\perp, \quad \mathsf{S} \subset \mathsf{R}^\perp. \tag{3.56}$$

Since in view of (3.35), (3.37), (3.44) and (3.46) each $p^0 \in \mathsf{R}^0$ uniquely determines a $p \in \mathsf{R}$ and vice versa, the spaces R^0 and R are isomorphic. So we have

$$\dim \mathsf{R} = \dim \mathsf{R}^0 = k + l - g; \tag{3.57}$$

similarly:

$$\dim \mathsf{S} = \dim \mathsf{S}^0 = k + l - h. \tag{3.58}$$

From (3.45), (3.57) and (3.58) it follows that

$$\dim \mathsf{S}^{\perp} = \dim \mathsf{Q} - \dim \mathsf{S} = k + l - g = \dim \mathsf{R}. \tag{3.59}$$

Similarly:

$$\dim \mathsf{R}^{\perp} = \dim \mathsf{S}. \tag{3.60}$$

These results in combination with (3.56) imply that

$$\mathsf{R} = \mathsf{S}^{\perp} \quad \text{and} \quad \mathsf{S} = \mathsf{R}^{\perp}. \tag{3.61}$$

Since $(\ker D)^{\perp} = D^*(\mathsf{P})$, we obtain from (3.51) and (3.61):

$$\mathsf{R} = D^*(\mathsf{P}); \tag{3.62}$$

similarly:

$$\mathsf{S} = C^*(\mathsf{Q}). \tag{3.63}$$

In these equations D^* and C^* are the mappings dual to D and C, respectively. From (3.62) and (3.50) it follows that

$$CD^* = 0. \tag{3.64}$$

Similarly:

$$DC^* = 0. \tag{3.65}$$

The ranks of the mappings C and D are:

$$r(C) = r(C^*) = \dim \mathsf{S} = k + l - h, \tag{3.66}$$

$$r(D) = r(D^*) = \dim \mathsf{R} = k + l - g. \tag{3.67}$$

For later use we define arbitrary spaces $\bar{\mathsf{P}}$ and $\bar{\mathsf{Q}}$ such that

$$\mathsf{P} = \bar{\mathsf{P}} \oplus \ker D^*, \tag{3.68}$$

$$\mathsf{Q} = \bar{\mathsf{Q}} \oplus \ker C^*. \tag{3.69}$$

The dimensions of these spaces are

$$\dim \bar{\mathsf{P}} = k + l - g, \tag{3.70}$$

$$\dim \bar{\mathsf{Q}} = k + l - h. \tag{3.71}$$

This can be proved as follows:
$\dim(\ker D^*) = \dim \mathsf{P} - \dim D^*(\mathsf{P}) = \dim \mathsf{P} - \dim \mathsf{R}$, so by (3.68) and (3.57) $\dim \bar{\mathsf{P}} = \dim \mathsf{R} = k + l - g$, which proves (3.70).
(3.71) can be proved in the same way.

The spaces $\bar{\mathsf{P}}$ and $\bar{\mathsf{Q}}$ are dual to $D(\mathsf{Q})$ and $C(\mathsf{P})$, respectively. The duality of the spaces $\bar{\mathsf{P}}$ and $D(\mathsf{Q})$ follows from the fact that $D(\mathsf{Q})^{\perp} \cap \bar{\mathsf{P}} = \{0\}$. Since $D(\mathsf{Q})^{\perp} = \ker D^*$ and by (3.68) $\ker D^* \cap \bar{\mathsf{P}} = \{0\}$. The duality of the spaces $\bar{\mathsf{Q}}$ and $C(\mathsf{P})$ can be proved in the same way.

By restricting the range of C from P to $C(\mathsf{P})$ we define the mapping

$$\bar{C}\colon \mathsf{P} \to C(\mathsf{P}). \tag{3.72}$$

Similarly we define the mapping

$$\bar{D}\colon \mathsf{Q} \to D(\mathsf{Q}). \tag{3.73}$$

The duality of the spaces $C(\mathsf{P})$ and $\bar{\mathsf{Q}}$ and of $D(\mathsf{Q})$ and $\bar{\mathsf{P}}$ just established implies the existence of the dual mappings

$$\bar{C}^*\colon \bar{\mathsf{Q}} \to \mathsf{Q}, \tag{3.74}$$

$$\bar{D}^*\colon \bar{\mathsf{P}} \to \mathsf{P}. \tag{3.75}$$

These mappings turn out to be just the restrictions

$$\bar{C}^* = C = |_{\bar{\mathsf{Q}}}, \tag{3.76}$$

$$\bar{D}^* = D^*|_{\bar{\mathsf{P}}}. \tag{3.77}$$

In order to prove (3.76) we note that for any $p \in \mathsf{P}$ and $\overline{\mathrm{d}q} \in \bar{\mathsf{Q}}$ we have $p(\bar{C}^*\overline{\mathrm{d}q} - C^*\,\overline{\mathrm{d}q}) = (\bar{C}p - Cp)\,\overline{\mathrm{d}q} = 0$. So $\bar{C}^*\,\overline{\mathrm{d}q} = C^*\,\overline{\mathrm{d}q}$, which proves (3.76). (3.77) can be proved in the same way.

By (3.69) and (3.76) the mapping $\bar{C}^*$ is regular on $\bar{\mathsf{Q}}$. So for any vector $\mathrm{d}q \in \mathsf{S}$ a unique vector $\overline{\mathrm{d}q} \in \bar{\mathsf{Q}}$ exists such that

$$\mathrm{d}q = \bar{C}^*\,\overline{\mathrm{d}q}. \tag{3.78}$$

Similarly for any vector $p \in \mathsf{R}$ a unique vector $\bar{p} \in \bar{\mathsf{P}}$ exists such that

$$p = \bar{D}^*\bar{p}. \tag{3.79}$$

Concluding this section we discuss how the spaces R and S are situated with respect to the spaces P^{t}, P^{e}, P^{d} and Q^{t}, Q^{e}, Q^{d}, respectively. This subject is connected with the possible existence of what will be called 'free' and 'frozen' variables.

If as a consequence of the constraints on the force variables the vector p^{t} is not allowed to lie in some i-dimensional subspace of P^{t}, we say that a number i of the p^{t} variables are frozen: they cannot change in any process which is compatible with the constraints. If on the other hand the intersection $\mathsf{R} \cap \mathsf{P}^{\mathrm{t}}$ is a j-dimensional subspace of R, the vectors p^{t} which lie in that part of R can take any value, irrespective of what the value of p^{e} and p^{d} might be. In that case we say that a number j of the p^{t} variables are free. Similar definitions will be used in connection with the external dissipative p variables and also in connection with the $\mathrm{d}q$ variables.

We now define mappings C^{t}: $\mathsf{P}^{t} \to \mathsf{P}$, C^{e}: $\mathsf{P}^{e} \to \mathsf{P}$, C^{d}: $\mathsf{P}^{d} \to \mathsf{P}$ as the restrictions

$$C^{t} = C|_{\mathsf{P}^{t}}, \quad C^{e} = C|_{\mathsf{P}^{e}}, \quad C^{d} = C|_{\mathsf{P}^{d}}. \tag{3.80}$$

The dual C^{t*}: $\mathsf{Q} \to \mathsf{Q}^{t}$ of the mapping C^{t} has the property

$$C^{t*}\,\mathrm{d}q = (C^{*}\,\mathrm{d}q)^{t}, \tag{3.81}$$

where the superscript t is used in accordance with the notation (3.47). Eq. (3.81) can be proved as follows. For all $p \in \mathsf{P}$ and $\mathrm{d}q \in \mathsf{Q}$ we have by definition:

$$p(C^{*}\,\mathrm{d}q) = (Cp)\,\mathrm{d}q. \tag{3.82}$$

So if $p = -p^{t} \in \mathsf{P}^{t}$, we have:

$$p^{t}(C^{*}\,\mathrm{d}q) = (Cp^{t})\,\mathrm{d}q. \tag{3.83}$$

By (3.80) and the orthogonality of the spaces Q^{e} and Q^{d} to P^{t} this may also be written as

$$p^{t}(C^{*}\,\mathrm{d}q)^{t} = (C^{t}p^{t})\,\mathrm{d}q. \tag{3.84}$$

From the definition of C^{t*} it then follows that

$$p^{t}(C^{*}\,\mathrm{d}q)^{t} = p^{t}(C^{t*}\,\mathrm{d}q) \tag{3.85}$$

and from this equation we finally obtain (3.81). Since $C^{*}(\mathsf{Q}) = \mathsf{S}$ is the space available to the vector $\mathrm{d}q$, $(C^{*}(\mathsf{Q}))^{t}$ is the space available to the vector $\mathrm{d}q^{t}$. By (3.81) this space is also given by $C^{t*}(\mathsf{Q})$. In the case of frozen $\mathrm{d}q^{t}$ variables we have $C^{t*}(\mathsf{Q}) \neq \mathsf{Q}^{t}$, and therefore $r(C^{t}) = r(C^{t*}) < k$, which implies that $\dim(\ker C^{t}) = \dim \mathsf{P}^{t} - r(C^{t}) > 0$. In that case $\mathsf{R} = \ker C$ has a non-trivial intersection with P^{t}, which means that there are free p^{t} variables. We thus see that frozen $\mathrm{d}q^{t}$ variables and free p^{t} variables always occur simultaneously. Similar results can be obtained for the reversed case and also for the case of external and dissipative variables. From the way in which the dissipative variables have been constructed it follows that free and therefore also frozen dissipative variables cannot exist. Suppose, in order to prove this, that $p \in \mathsf{R} \cap \mathsf{P}^{d}$, so $p \in \mathsf{P}^{d}$, which by (3.44) and (3.46) implies that $p^{0} = 0$. By (3.35) and (3.37) we then have $p^{d} = 0$, so $p = 0$. This means that $\mathsf{R} \cap \mathsf{P}^{d} = \{0\}$, which proves the non-existence of free dissipative force variables. The non-existence of free dissipative displacement variables can be proved in the same way.

In addition, in this paper free and frozen thermodynamic and external variables will be assumed to absent, so we have:

$$\mathsf{R} \cap \mathsf{P}^{\mathrm{t}} = \{0\}, \tag{3.86}$$

$$\mathsf{R} \cap \mathsf{P}^{\mathrm{e}} = \{0\}, \tag{3.87}$$

$$\mathsf{R} \cap \mathsf{P}^{\mathrm{d}} = \{0\} \tag{3.88}$$

and

$$\mathsf{S} \cap \mathsf{Q}^{\mathrm{t}} = \{0\}, \tag{3.89}$$

$$\mathsf{S} \cap \mathsf{Q}^{\mathrm{e}} = \{0\}, \tag{3.90}$$

$$\mathsf{S} \cap \mathsf{Q}^{\mathrm{d}} = \{0\}. \tag{3.91}$$

The assumed absence of frozen thermodynamic and external variables is in accordance with the assumptions on which the inequalities (3.15) were based. These inequalities in fact can be easily derived from the relations (3.86), (3.87), (3.89) and (3.90).

4. Constitutive equations

Since by definition the external variables are the variables by which the system is coupled to its environment, it is important to have explicit relations between the variables p^{e} and $\mathrm{d}q^{\mathrm{e}}$ in which the p^{t}, p^{d}, $\mathrm{d}q^{\mathrm{t}}$ and $\mathrm{d}q^{\mathrm{d}}$ variables do not occur. These relations will be called constitutive equations. If such an equation is stated as an expression which is explicit in p^{e}, we will call it the relaxational form and if it is explicit in $\mathrm{d}q^{\mathrm{e}}$, the retardational form of the constitutive equation.

In order to obtain constitutive equations the thermodynamic equations of state (2.5), which relate the thermodynamic variables to each other and equations that relate the dissipative variables to each other are needed. The latter will be called rate equations. Since in these equations time derivatives occur, instead of differentials we have to use time derivatives. These will be achieved simply by giving from now on the differential operator d, the meaning of a time derivative:

$$\mathrm{d} = \frac{\mathrm{d}}{\mathrm{d}t}. \tag{4.1}$$

In most cases this operator can be treated as a scalar factor; expressions such as

$$f = \frac{1}{1 + \tau d} g, \tag{4.2}$$

where f and g are functions of time, are equivalent therefore to the corresponding differential equations; in this case

$$f + \tau \frac{\mathrm{d}f}{\mathrm{d}t} = g. \tag{4.3}$$

For further details about the properties of the operator d we refer to Chapter 2 and Appendix 6 of ref. 15.

By differentiating the equations of state (2.5) we obtain:

$$\mathrm{d}p^{\mathrm{t}} = A^{\mathrm{t}}\,\mathrm{d}q^{\mathrm{t}}, \tag{4.4}$$

where

$$A^{\mathrm{t}} = \frac{\partial p^{\mathrm{t}}}{\partial q^{\mathrm{t}}} \tag{4.5}$$

is a linear mapping $A^{\mathrm{t}}: \mathsf{Q}^{\mathrm{t}} \to \mathsf{P}^{\mathrm{t}}$. From elementary thermodynamic considerations it follows that A^{t} is self-adjoint (Maxwell relations) and positive definite (stability conditions, see for instance ref. 14, Chapter 8); so we have:

$$(A^{\mathrm{t}}\,\mathrm{d}q^{\mathrm{t}})\,\mathrm{d}\tilde{q}^{\mathrm{t}} = (A^{\mathrm{t}}\,\mathrm{d}\tilde{q}^{\mathrm{t}})\,\mathrm{d}q^{\mathrm{t}} \tag{4.6}$$

and

$$(A^{\mathrm{t}}\,\mathrm{d}q^{\mathrm{t}})\,\mathrm{d}q^{\mathrm{t}} > 0 \quad \forall\, \mathrm{d}q^{\mathrm{t}} \neq 0. \tag{4.7}$$

As usual in non-equilibrium thermodynamics we consider the case of linear rate equations; so we have

$$p^{\mathrm{d}} = B^{\mathrm{d}}\,\mathrm{d}q^{\mathrm{d}}, \tag{4.8}$$

where $B^{\mathrm{d}}: \mathsf{Q}^{\mathrm{d}} \to \mathsf{P}^{\mathrm{d}}$ is a non-singular linear mapping. This mapping is as a consequence of the Onsager symmetry relations self-adjoint:

$$(B^{\mathrm{d}}\,\mathrm{d}q^{\mathrm{d}})\,\mathrm{d}\tilde{q}^{\mathrm{d}} = (B^{\mathrm{d}}\,\mathrm{d}\tilde{q}^{\mathrm{d}})\,\mathrm{d}q^{\mathrm{d}}. \tag{4.9}$$

Furthermore, by the second law of thermodynamics we have:

$$T\,\mathrm{d}_{\mathrm{i}}S = (B^{\mathrm{d}}\,\mathrm{d}q^{\mathrm{d}})\,\mathrm{d}q^{\mathrm{d}} > 0 \quad \forall\, \mathrm{d}q^{\mathrm{d}} \neq 0. \tag{4.10}$$

So the mapping B^{d} is positive definite.
In general the mapping B^{d} will depend on the thermodynamic variables of state. For simplicity in this paper only the case of a constant B^{d} will be considered, however. In that case by differentiating (4.9) we obtain:

$$\mathrm{d}p^{\mathrm{d}} = (B^{\mathrm{d}}\mathrm{d})\,\mathrm{d}q^{\mathrm{d}}. \tag{4.11}$$

For later use some mappings related to A^{t} and B^{d} will be introduced now.

First we extend the mapping $A^t\colon \mathsf{Q}^t \to \mathsf{P}^t$ to $A\colon \mathsf{Q} \to \mathsf{P}$ by defining

$$A^t = A\Big|_{\mathsf{Q}^t} \quad \text{and} \quad A(\mathsf{Q}^e \oplus \mathsf{Q}^d) = 0. \tag{4.12}$$

Similarly $(A^t)^{-1}\colon \mathsf{P}^t \to \mathsf{Q}^t$ is extended to $A^-\colon \mathsf{P} \to \mathsf{Q}$, defined by

$$(A^t)^{-1} = A^-\Big|_{\mathsf{P}^t} \quad \text{and} \quad A^-(\mathsf{P}^e \oplus \mathsf{P}^d) = 0. \tag{4.13}$$

In a similar way we define the mappings

$$B\colon \mathsf{Q} \to \mathsf{P} \tag{4.14}$$

and

$$B^-\colon \mathsf{P} \to \mathsf{Q} \tag{4.15}$$

as extensions of B^d and $(B^d)^{-1}$, respectively. Finally we define the mappings $M\colon \mathsf{Q} \to \mathsf{P}$ and $N\colon \mathsf{P} \to \mathsf{Q}$ as

$$M = A + Bd, \tag{4.16}$$

$$N = A^- + \frac{B^-}{d}. \tag{4.17}$$

The mappings M and N are non-singular on respectively S and R. This can be proved as follows. A and B are non-singular on Q^t and Q^d, respectively; so from (4.17) and the definitions of A and B we obtain:

$$\ker M = \mathsf{Q}^e. \tag{4.18}$$

Similarly:

$$\ker N = \mathsf{P}^e, \tag{4.19}$$

Using (3.90) and (3.87) respectively we obtain:

$$(\ker M) \cap \mathsf{S} = \{0\}, \tag{4.20}$$

$$(\ker N) \cap \mathsf{R} = \{0\}, \tag{4.21}$$

which proves the non-singularity of the mappings M and N on S and R, respectively.

M is also positive definite on S, since by (4.6), (4.7), (4.16) and the definitions of A and B, we have for any $\mathrm{d}q \in \mathsf{S}$ that $(M\,\mathrm{d}q)\,\mathrm{d}q > 0$. Similarly N is positive definite on R.

The spaces R and $M(\mathsf{S})$ just span the whole space P:

$$\mathsf{P} = \mathsf{R} \oplus M(\mathsf{S}). \tag{4.22}$$

Similarly:

$$\mathsf{Q} = \mathsf{S} \oplus N(\mathsf{R}). \tag{4.23}$$

This can be proved as follows. If for any non-zero $\mathrm{d}q \in \mathsf{S}$ it would apply that $\mathrm{d}p = M\,\mathrm{d}q \in M(\mathsf{S}) \cap \mathsf{R}$, then $\mathrm{d}p \in \mathsf{R}$ and by (3.61) $\mathrm{d}p\,\mathrm{d}q = (M\,\mathrm{d}q)\,\mathrm{d}q = 0$, which is in contradiction with the positive definiteness of M on S. So we obtain:

$$M(\mathsf{S}) \cap \mathsf{R} = \{0\}. \tag{4.24}$$

On the other hand, since $\dim M(\mathsf{S}) = \dim \mathsf{S} = k + l - h$ and $\dim \mathsf{R} = k + l - g$, the sum of the dimensions of $M(\mathsf{S})$ and R just equals the dimension of P. This, in combination with result (4.24), proves (4.22). In a similar way (4.23) may be proved.

With the aid of the constraint equations we now are able to derive the constitutive equations. To this end we substitute (4.4) and (4.11) in the identity

$$\mathrm{d}p = -\mathrm{d}p^{\mathrm{t}} + \mathrm{d}p^{\mathrm{e}} - \mathrm{d}p^{\mathrm{d}} \tag{4.25}$$

and obtain:

$$\mathrm{d}p = -A^{\mathrm{t}}\,\mathrm{d}q^{\mathrm{t}} + \mathrm{d}p^{\mathrm{e}} - (B^{\mathrm{d}}d)\,\mathrm{d}q^{\mathrm{d}} \tag{4.26}$$

or equivalently:

$$\mathrm{d}p = -(A + Bd)\,\mathrm{d}q + \mathrm{d}p^{\mathrm{e}}, \tag{4.27}$$

which by (4.16) becomes:

$$\mathrm{d}p + M\,\mathrm{d}q = \mathrm{d}p^{\mathrm{e}}. \tag{4.28}$$

On multiplying by $\bar{C}$ and making use of (3.48) we obtain:

$$\bar{C}M\,\mathrm{d}q = \bar{C}\,\mathrm{d}p^{\mathrm{e}}. \tag{4.29}$$

With (3.78) this may be written as

$$\bar{C}M\bar{C}^*\,\overline{\mathrm{d}q} = \bar{C}\,\mathrm{d}p^{\mathrm{e}}. \tag{4.30}$$

The mapping $\bar{C}M\bar{C}^*$ is regular on $\bar{Q}$, since $\bar{C}^*$ by (3.69) and (3.76) is regular on $\bar{\mathsf{Q}}$, M is regular on $\mathsf{S} = \bar{C}^*(\bar{\mathsf{Q}})$ and $\bar{C}$ is regular on $M(\mathsf{S})$ since by (4.24) and (3.50) $M(\mathsf{S}) \cap \ker \bar{C} = \{0\}$. So this mapping may be inverted and from (4.30) and (3.78) we obtain:

$$\mathrm{d}q = \bar{C}^*(\bar{C}M\bar{C}^*)^{-1}\bar{C}\,\mathrm{d}p^{\mathrm{e}}. \tag{4.31}$$

Since in any specific case $\mathrm{d}q^{\mathrm{e}}$ can easily be obtained from $\mathrm{d}q$, an explicit relation between $\mathrm{d}q^{\mathrm{e}}$ and $\mathrm{d}p^{\mathrm{e}}$ is contained in (4.31). So we have obtained a formal expression of the constitutive equation in its retardational form.

In a similar way it can be shown that the formal expression for the constitutive equation in its relaxational form reads:

$$\mathrm{d}p = \bar{D}^*(\bar{D}N\bar{D}^*)^{-1}\bar{D}\,\mathrm{d}q^{\mathrm{e}}. \tag{4.32}$$

5. Canonical forms of the mappings M and N

The special properties of the mappings A^{t} and B^{d}, mentioned in the preceding section, enable us to obtain rather simple matrix representations of the mappings M and N. In order to derive such a representation for the mapping M we decompose the space S as follows:

$$\mathsf{S} = \mathsf{S}_1 \oplus \mathsf{S}_2 \oplus \mathsf{S}_3, \tag{5.1}$$

where

$$\mathsf{S}_1 = \mathsf{S} \cap (\mathsf{Q}^{\mathrm{t}} \oplus \mathsf{Q}^{\mathrm{e}}), \tag{5.2}$$

$$\mathsf{S}_2 = \mathsf{S} \cap (\mathsf{Q}^{\mathrm{e}} \oplus \mathsf{Q}^{\mathrm{d}}) \tag{5.3}$$

and where S_3 is any complement of $\mathsf{S}_1 \oplus \mathsf{S}_2$ in S. Such a decomposition is possible since

$$\mathsf{S}_1 \cap \mathsf{S}_2 = \mathsf{S} \cap (\mathsf{Q}^{\mathrm{t}} \oplus \mathsf{Q}^{\mathrm{e}}) \cap \mathsf{S} \cap (\mathsf{Q}^{\mathrm{e}} \oplus \mathsf{Q}^{\mathrm{d}}) = \mathsf{S} \cap \mathsf{Q}^{\mathrm{e}} = \{0\}, \tag{5.4}$$

where (3.90) has been used.

The dimensions of the spaces S_1, S_2 and S_3 are:

$$\dim \mathsf{S}_1 = g, \tag{5.5}$$

$$\dim \mathsf{S}_2 = l - h, \tag{5.6}$$

$$\dim \mathsf{S}_3 = k - g. \tag{5.7}$$

Eq. (5.5) can be proved as follows:

$$\begin{aligned}\dim \mathsf{S}_1 &= \dim \mathsf{S} \cap (\mathsf{Q}^{\mathrm{t}} \oplus \mathsf{Q}^{\mathrm{e}}) \\ &= \dim \mathsf{S} + \dim(\mathsf{Q}^{\mathrm{t}} \oplus \mathsf{Q}^{\mathrm{e}}) - \dim(\mathsf{S} + (\mathsf{Q}^{\mathrm{t}} \oplus \mathsf{Q}^{\mathrm{e}})) \\ &= k + l - h + k + l - (k + l + m) = g.\end{aligned}$$

Here we have used the fact that $\mathsf{S} + (\mathsf{Q}^{\mathrm{t}} \oplus \mathsf{Q}^{\mathrm{e}}) = \mathsf{Q}$, which is a consequence of the fact that by the assumption of the absence of frozen variables the whole space Q^{d} is available to the $\mathrm{d}q^{\mathrm{d}}$ component of $\mathrm{d}q$. The proof of eq. (5.6) is similar to that of (5.5). Finally

$$\begin{aligned}\dim \mathsf{S}_3 &= \dim \mathsf{S} - \dim \mathsf{S}_1 - \dim \mathsf{S}_2 \\ &= k + l - h - g - (l - h) = k - g,\end{aligned}$$

which proves (5.7).

Note that since in $Q^t \oplus Q^e$ the vector dq equals dq^0 and since S^0 is the space available to vectors $dq^0 \in Q^t \oplus Q^e$, $S_1 = S \cap (Q^t \oplus Q^e)$ is a subspace of S^0. In fact S_1 is the subspace of S^0 of vectors for which $dq^d = 0$, so $S_1 = R^{0\perp}$. From this relation and (3.40) the result (5.5) is obtained again.

The decomposition (5.1) is convenient for our purpose since for arbitrary $dq \neq 0$ we have

$$\text{on } S_1\text{: } (A\,dq)\,dq > 0, \quad (B\,dq)\,dq = 0, \tag{5.8}$$

$$\text{on } S_2\text{: } (A\,dq)\,dq = 0, \quad (B\,dq)\,dq > 0, \tag{5.9}$$

$$\text{on } S_3\text{: } (A\,dq)\,dq > 0, \quad (B\,dq)\,dq > 0. \tag{5.10}$$

The first statement (5.8) follows from the fact that A is positive definite on Q^t and $dq^t \neq 0$ for every nonzero $dq \in S_1$; the latter is a consequence of the fact that by (3.90) $S \cap Q^e = \{0\}$. The second statement (5.8) follows from the fact that B vanishes on Q^t and Q^e and that by (5.2) dq^d vanishes for every $dq \in S_1$. The statements (5.9) and (5.10) can be proved in a similar way. From the results (5.8)–(5.10) it follows that a basis $\{s_i\} \in S$ may be chosen, such that

$$\text{on } S_1\text{: } \hat{A}_{ij} = \delta_{ij}, \quad \hat{B}_{ij} = 0, \tag{5.11}$$

$$\text{on } S_2\text{: } \hat{A}_{ij} = 0, \quad \hat{B}_{ij} = \delta_{ij}, \tag{5.12}$$

$$\text{on } S_3\text{: } \hat{A}_{ij} = \delta_{ij}, \quad \hat{B}_{ij} = t_i\delta_{ij}, \tag{5.13}$$

where

$$\hat{A}_{ij} = (A\hat{s}_j)\hat{s}_i \tag{5.14}$$

and $\hat{B}_{ij} = (B\hat{s}_j)\hat{s}_i$. (5.15)

The matrices with elements defined by (5.14) and (5.15) will be denoted by $(\hat{A})$ and $(\hat{B})$. These are also the matrix representations of the mappings $A|_S$ and $B|_S$ with respect to the basis $\{s_i\} \in S$ and dual bases in $A(S)$ and $B(S)$, respectively.

The quantities $t_i > 0$, which will be called retardation times, are the non-zero roots of the characteristic equation

$$\det(t[A] - [B]) = 0, \tag{5.16}$$

where A and B are matrices with elements defined analogously to (5.14) and (5.15) with respect to an arbitrary basis in S.

By (4.16) and (5.11)–(5.13) the matrix representation of the operator $M|_S$ with respect to the $\{s_i\}$ basis in S becomes:

$$[\hat{M}_{ij}] = \operatorname{diag}\underbrace{(1, \ldots, 1;}_{g}\ \underbrace{d, \ldots, d;}_{l-h}\ \underbrace{1 + t_1 d, \ldots, 1 + t_{k-g} d).}_{k-g} \tag{5.17}$$

The numbers of diagonal elements of the various types correspond to the dimensions of the spaces S_1, S_2 and S_3, given in eqs. (5.5)–(5.7).

Analogously to (5.17) the mapping N, defined in (4.17), has the following canonical form:

$$[\hat{N}_{ij}] = \operatorname{diag}\Big(\underbrace{1, \dots, 1}_{h};\ \underbrace{\frac{1}{d}, \dots, \frac{1}{d}}_{l-g};\ \underbrace{1+\frac{1}{\tau_1 d}, \dots, 1+\frac{1}{\tau_{k-h} d}}_{k-h}\Big). \tag{5.18}$$

This form is obtained on subdividing the space R as follows:

$$\mathsf{R} = \mathsf{R}_1 \oplus \mathsf{R}_2 \oplus \mathsf{R}_3, \tag{5.19}$$

where

$$\mathsf{R}_1 = \mathsf{R} \cap (\mathsf{P}^t \oplus \mathsf{P}^e), \tag{5.20}$$

$$\mathsf{R}_2 = \mathsf{R} \cap (\mathsf{P}^e \oplus \mathsf{P}^d), \tag{5.21}$$

$$\mathsf{R}_3 = \text{any complement of } \mathsf{R}_1 \oplus \mathsf{R}_2 \text{ in } \mathsf{R}. \tag{5.22}$$

It can be proved that

$$\dim \mathsf{R}_1 = h, \tag{5.23}$$

$$\dim \mathsf{S}_2 = l - g, \tag{5.24}$$

$$\dim \mathsf{S}_3 = k - h. \tag{5.25}$$

The quantities $\tau_i > 0$ in (5.18), which will be called relaxation times, are the non-zero roots of the characteristic equation

$$\det([A^-] - \tau[B^-]) = 0, \tag{5.26}$$

where the matrices $[A^-]$ and $[B^-]$ are defined similarly to $[A]$ and $[B]$ in (5.16) with respect to an arbitrary basis in R.

6. Canonical forms of the constitutive equations

The results obtained in the preceding section enable us to derive more explicit forms of the constitutive equations (4.31) and (4.32).

We use a matrix notation in which all vectors are represented by column matrices. In particular:

$$[p]=\begin{bmatrix} -p_1^{\mathrm{t}} \\ \vdots \\ -p_k^{\mathrm{t}} \\ p_1^{\mathrm{e}} \\ \vdots \\ p_l^{\mathrm{e}} \\ -p_1^{\mathrm{d}} \\ \vdots \\ -p_m^{\mathrm{d}} \end{bmatrix}, \quad [\mathrm{d}q]=\begin{bmatrix} \mathrm{d}q_1^{\mathrm{t}} \\ \vdots \\ \mathrm{d}q_k^{\mathrm{t}} \\ \mathrm{d}q_1^{\mathrm{e}} \\ \vdots \\ \mathrm{d}q_l^{\mathrm{e}} \\ \mathrm{d}q_1^{\mathrm{d}} \\ \vdots \\ \mathrm{d}q_m^{\mathrm{d}} \end{bmatrix}. \tag{6.1}$$

A mapping, such as C: $\mathsf{P} \to \mathsf{P}$, will with respect to a basis $\{e_i\} \in \mathsf{R}$ be represented by a matrix $[C_{ij}]$, also denoted by $[C]$, such that $Ce_j = \Sigma_i C_{ij} e_i$. We also have:

$$C_{ij} = (Ce_j)f_i = e_j(C^* f_i) = C^*_{ji}, \tag{6.2}$$

in which $\{f_i\} \in \mathsf{Q}$ is the basis dual to the basis $\{e_j\} \in \mathsf{P}$.

From (6.2) we see that in the present notation the matrix of the dual of a mapping is the transposed of the matrix of the mapping itself:

$$[C^*] = [C]^{\mathrm{T}}. \tag{6.3}$$

Analogously to C^0 the mapping C is determined only up to premultiplication by an arbitrary non-singular mapping [see the statements below eq. (3.12)]. Therefore, since any $n \times n$ matrix of rank r can by premultiplication by a suitable non-singular matrix be brought into a form in which its last $(n-r)$ rows are zero, without loss of generality it may be assumed that the matrix $[C]$ has the form

$$[C]=\begin{bmatrix} \times & \times & \cdots & \times \\ \vdots & & & \vdots \\ \times & \cdots & \cdots & \times \\ 0 & 0 & \cdots & 0 \\ \vdots & & & \vdots \\ 0 & \cdots & \cdots & 0 \end{bmatrix} \begin{matrix} \left.\vphantom{\begin{matrix}a\\a\\a\end{matrix}}\right\} k+l-h \\ \left.\vphantom{\begin{matrix}a\\a\\a\end{matrix}}\right\} k+l-g \end{matrix} \tag{6.4}$$

In that case $C(\mathsf{P})$ is the space spanned by the base vectors $e_1, \ldots, e_{k+l-h}$.

The matrix representation of the mapping $\bar{C}$: $\mathsf{P} \to C(\mathsf{P})$ with respect to the $\{e_i\}$ bases in P and $C(\mathsf{P})$ is just given then by the non-zero rows of $[C]$. Since the matrix of C^*: $\mathsf{Q} \to \mathsf{Q}$ is given by $[C^*] = [C]^{\mathrm{T}}$, from (6.4) we see that the base vectors $f_{k+l-h+1}, \ldots, f_{k+l+m}$ just span the space $\ker C^*$. So by (3.69) the space Q may be chosen to be the space spanned by the base vectors $f_1, \ldots, f_{k+l-h}$.

The matrix of $\bar{C}^*: \bar{Q} \to Q$ is given by then by $[\bar{C}^*] = [\bar{C}]^T$. The constitutive equation (4.31) becomes in matrix form:

$$[dq] = [\bar{C}]^T([\bar{C}][M][\bar{C}]^T)^{-1}[\bar{C}][dp^e]. \tag{6.5}$$

Here (M) is the $(k+l+m) \times (k+l+m)$ matrix of the mapping $M: Q \to P$ with respect to the $\{e_i\} \in P$ and $\{f_i\} \in Q$ bases.

From the preceding section we know that a basis $\{\hat{s}_i\} \in S$ exists such that the matrix $[\hat{M}]$ of elements $M_{ij} = (M\hat{s}_j)\hat{s}_i$ has the canonical form (5.17). A unique vector $\bar{s}_i \in \bar{Q}$ corresponds with each vector $\hat{s}_i \in S$, by (3.78), such that

$$\hat{s}_i = \bar{C}^* \bar{s}_i. \tag{6.6}$$

So we have:

$$\hat{M}_{ij} = M(\bar{C}^* \bar{s}_j)\bar{C}^* \bar{s}_i = (\bar{C}M\bar{C}^* \bar{s}_j)\bar{s}_i. \tag{6.7}$$

We thus see that the mapping $\bar{C}M\bar{C}$ has the same matrix representation $[\hat{M}]$ with respect to the $\{s_i\}$ basis in $\bar{Q}$ as M has with respect to the $\{\hat{s}_i\}$ basis in S. If (Φ) is the non-singular matrix (with elements Φ_{ik}) of the transformation

$$\bar{s}_i = \sum_k \Phi_{ik} f_k, \quad (i, k = 1, \ldots, k+l-h), \tag{6.8}$$

it follows that

$$[\Phi][\bar{C}][M][\bar{C}]^T[\Phi]^T = [\hat{M}], \tag{6.9}$$

so if

$$[\hat{C}] = [\Phi][\bar{C}] \tag{6.10}$$

we have

$$[\hat{C}][M][\hat{C}]^T = [\hat{M}]. \tag{6.11}$$

Substitution of (6.10) and (6.11) into (6.5) gives:

$$[dq] = [\hat{C}]^T[\hat{M}]^{-1}[\hat{C}][dp^e]. \tag{6.12}$$

If finally we introduce matrices $[J]^\mu$ with elements

$$J^\mu_{im} = \hat{C}_{\mu i}\hat{C}_{\mu m}, \tag{6.13}$$

(6.12) can be written with the aid of (5.17) as

$$[dq] = \left\{ \sum_{\alpha=1}^{g} [J]^\alpha + \sum_{\beta=1}^{l-h} \frac{[J]^\beta}{d} + \sum_{\gamma=1}^{k-g} \frac{[J]^\gamma}{1+t_\gamma d} \right\} [dp^e]. \tag{6.14}$$

A similar reasoning starting from the relaxational form (4.32) of the constitutive equation leads to

$$[\mathrm{d}p] = \left\{\sum_{\alpha=1}^{h} [G]^{\alpha} + \sum_{\beta=1}^{l-g} [G]^{\beta} d + \sum_{\gamma=1}^{k-h} \frac{[G]^{\gamma}\tau_{\gamma} d}{1+\tau_{\gamma} d}\right\}[\mathrm{d}q^{\mathrm{e}}]. \tag{6.15}$$

Here the elements of the matrices $[G]^{\mu}$ are given by

$$G^{\mu}_{im} = \hat{D}_{\mu i}\hat{D}_{\mu m}, \tag{6.16}$$

where

$$[\hat{D}] = [\Psi][D];$$

$[\Psi]$ is a non-singular transformation matrix, such that

$$[\hat{D}][N][\hat{D}]^{\mathrm{T}} = [\hat{N}],$$

where $[\hat{N}]$ is given by (5.18).

If zero initial conditions are assumed at time $t = -\infty$, eqs. (6.14) and (6.15) can be integrated to

$$[q(t)] = \int_{-\infty}^{t} [J(t-\tau)][\dot{p}(\tau)^{\mathrm{e}}]\,\mathrm{d}\tau, \tag{6.19}$$

$$[p(t)] = \int_{-\infty}^{t} [G(t-\tau)][\dot{q}(\tau)^{\mathrm{e}}]\,\mathrm{d}\tau, \tag{6.20}$$

the after effect representations of the constitutive equations. Here a superimposed dot denotes a differentiation with respect to time and

$$[J(t)]\sum_{\alpha=1}^{g} [J]^{\alpha} + \sum_{\beta=1}^{l-h} [J]^{\beta} t + \sum_{\gamma=1}^{k-g} [J]^{\gamma}(1-\mathrm{e}^{-t/t_{\gamma}}), \tag{6.21}$$

$$[G(t)] = \sum_{\alpha=1}^{h} [G]^{\alpha} + \sum_{\beta=1}^{l-g} [G]^{\beta}\delta(t) + \sum_{\gamma=1}^{k-h} [G]^{\gamma}\,\mathrm{e}^{-t/t_{\gamma}}. \tag{6.22}$$

These functions will be called the retardation and relaxation functions (matrices) of the system. From (6.19) and (6.20) it may be proved that these functions are proportional to the response of the system to a stimulus $[p(t)]$ or $[g(t)]$ respective of the form of a stepfunction.

7. Discussion

In this paper a theory is presented for describing the linear relaxational and retardational behaviour of thermodynamic systems. The theory is based upon an explicit distinguishment of two types of variables: the thermodynamic variables and the external ones and the introduction of relations between those two types of variables, the constraint equations (3.11) and (3.12). An important result is that the form of the retardation and the relaxation function of the system is determined by four fundamental integers: the number of thermodynamic variables of state k, the number of external variables l, the rank of the force-constraint matrix g and the rank of the displacement-constraint matrix h. The approach[1]) in which internal variables are used as well as the approach of Kluitenberg[2]) can be considered as special cases of the present formalism. In this formalism these two approaches correspond to two special choices of the thermodynamic variables of state, i.e. of the base vectors in the spaces P and Q^t; these two choices result in two different representations of the constraint equations.

By the introduction of constraint equations we explicitly distinguish between thermodynamic and structural properties of the system. This resembles the usual approach in the theory of electrical networks (see for instance ref. 16). In that theory equations are used representing the physical properties of elements of the network and in addition equations which solely represent its structure. The latter equations are equivalent to our equations (3.48) and (3.49); the matrices comparable with our matrices $[C]$ and $[D]$ are called the incidence matrix and the mesh matrix, respectively. These matrices, which are obtained from the graph of the network, obey orthogonality relations similar to our equations (3.64) and (3.65). In electrical network theory[17]) and also in a broader context[18]) these equations express a theorem known as Tellegen's theorem. In network theory this theorem can be proved with the aid of the Kirchoff's current and voltage laws from general assumptions on the topological structure of the network. In this derivation the dissipative elements of the network have to be introduced beforehand. Our derivation of the equations (3.64) and (3.65) was based upon the construction of the dissipative variables p^d and dq^d, described in section 3. In this derivation no assumptions on the topological structure of the system had to be made.

In concern with the applicability of the present theory we can say that the mathematical formalism is general enough to include all kinds of vectorial and tensorial phenomena. In applications to continuum mechanics for instance the scalar product $p^e \, dq^e$ may stand for $\boldsymbol{T} \cdot (\boldsymbol{F}^{-1}) : \boldsymbol{dF}$, where $\boldsymbol{T}$ is the Cauchy stress tensor and $\boldsymbol{F}$ is the deformation gradient. The scalar product in this case is the inner product in the space of cartesian tensors defined by

$$\boldsymbol{A} : \boldsymbol{B} = \mathrm{Tr}(\boldsymbol{A} \cdot \boldsymbol{B}^{\mathrm{T}}). \qquad (7.1)$$

In this case spaces P^e and Q^e coincide and are just the ordinary and three-dimensional Euclidian space.

The theory as presented here is essentially linear since we have restricted ourselves to the case that the mappings A, B, C and D can be treated as constants. Extensions to non-linear cases are possible, however, in several directions. An interesting possibility is to consider the case of time-dependent constraint equations. This corresponds to time-dependent structural changes of the system. On of the main features of our approach is that it offers the possibility of analyzing the influence of such structural changes upon the relaxational and retardational behaviour of a system in an explicit way.

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