Non-stationary thermodynamics of polarisable and magnetisable dissipative fluid media

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Abstract. A phenomenological theory is proposed of a charged, streaming N-component mixture of dissipative fluids which are polarisable and magnetisable and whose governing equations form an hyperbolic system. Non-stationary transport equations are proposed for dissipative fluxes containing new cross-effect terms, as required for compatibility with the entropy principle expressed by a new balance equation (including a new Gibbs equation). The theory formed by the set of $(13N+7)$ equations governing the material behaviour of the system, by generalising the constitutive equations of a quasineutral media, together with Maxwell's equations, may be referred to as the electrodynamics of dissipative, streaming media. Proposed transport laws for polarisation and magnetisation generalise the well-known Debye law for relaxation, and show the possible influence of temperature and density gradients on polarisation and magnetisation. The forms of the free energy and of the Gibbs function, in the non-stationary regime, are also formulated.

1. Introduction and formulation of the problem

During the last two decades a non-stationary thermodynamics has been developed, generalising the traditional non-equilibrium thermodynamics, which is stationary since it neglects, among other things, inertial effects of dissipative fluxes. Such a 'stationary theory' has only a limited range of validity and is in fact inadequate for a description of certain fast transition processes, such as wavefront motion. The aim of this paper is to show how non-stationary thermodynamics of fluids in the version given by Müller (1967), confirmed and complemented by Israel (1976) and generalised to elastic media by Kranyš (1977a, b), can be extended to polarisable and magnetisable multifluid dissipative systems.

We want to study an electromechanical system consisting of a charged, streaming N-component mixture of dissipative fluids which is polarisable and magnetisable and which is not far from thermodynamic equilibrium. In the state of thermodynamic equilibrium, the fluid mixture is supposed to be isotropic, electrically neutral ($\tilde{\rho} = 0$), not polarised or magnetised ($P^l = M^l = 0$) and therefore not subject to an electromagnetic field. This electromechanical system, in which thermodynamic dissipative processes are operative is, as a whole, taken to be a closed system, in the sense that conservation of linear momentum, angular momentum and energy within it will obtain. From this requirement, it follows, for example, that the pressure tensor of the mixture has to be symmetric ($\overset{*}{\pi}{}^{kl} = \overset{*}{\pi}{}^{lk}$). For the description of the electromagnetic field, the vectors E^l and B^l are regarded as basic, so one has to include within the vectors D^l and H^l any effect due to the presence of matter (cf Born and Wolf (1970) p 1).

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In this paper we want to consider our system as a non-relativistic one, which allows us to simplify slightly the formulae of electrodynamics in order that the whole theory conforms to 'Galilean relativity' (cf Penfield and Haus (1967) p 57). The relativistic theory is, no doubt, the only one physically strictly consistent for our case, and we will present this formalism in a later paper. (See note added in proof).

As we do not want to omit non-stationary phenomena from our description, we will investigate our system on the basis of non-stationary thermodynamics (applicable for the states of the system not far from thermodynamic equilibrium). The method of derivation of the transport equations is the same as in ordinary irreversible thermodynamics (which we call stationary thermodynamics). The only difference is that the non-stationary theory is based on a more general assumption, which allows the entropy density function s and also the entropy flux $\mathscr{S}^l$ to be dependent on the ordinary non-dissipative variables as well as on *all* dissipative fluxes. This results in a generalisation of the entropy balance equation where all terms of order two, O(2), are systematically retained.

The ordering of quantities is to be understood in the following way. All quantities in thermodynamic equilibrium which do not vanish are considered to be O(0); we consider all quantities to be O(1), which vanish at equilibrium together with all their space and time derivatives. Therefore, we always (see table 1) have

$$\rho, T, p, u, \underset{A}{c}, \overset{(0)}{\underset{A}{\mu}}, \dots \qquad \text{of O(0)} \tag{1.1}$$

and

$$\underset{A}{\pi}, \underset{A}{\pi}^{kl}, \underset{A}{h}^l, E^l, P^l, \dots \qquad \text{and} \qquad \dot{\rho}, \partial^l T, \partial^l \underset{A}{\pi}, \dots \qquad \text{of O(1).} \tag{1.2}$$

As an example, one has to ascribe different order to v^l and B^l depending on whether one supposes that, in thermodynamic equilibrium, the fluid velocity and magnetic field (A) do not vanish or (B) do vanish.

$$\text{In case } \begin{cases} \text{(A)} \\ \text{(B)} \end{cases} v^l \text{ and } B^l \text{ are of order } \begin{cases} \text{O(0)} \\ \text{O(1)} \end{cases}. \tag{1.3}$$

At the beginning we will admit (for heuristic reasons) the validity of alternative (A), but later we will limit ourselves to case (B) which means that the medium studied is immobile and isotropic (except for linear ('infinitesimal') perturbations)†. Because of

Table 1. Nomenclature used in this paper. We use SI units.

$\overset{*}{\pi}{}^{kl} = (p + \pi)\delta^{kl} + \pi^{kl} = $ pressure tensor	$\underset{A}{c} = \underset{A}{\rho}/\rho = $ mass fraction
$\pi = $ bulk viscous stress	$\overset{(0)}{\underset{A}{\mu}} = \underset{A}{w} - \underset{A}{s}^{(0)} T = $ chemical potential
$\pi^{kl} = $ shear viscous stress	$J^l = I^l - \tilde{\rho}v^l = $ conductive current
$v^l = $ fluid mixture velocity	$\tilde{\rho} = $ free charge density
$u = $ (specific) internal energy	$P^l = $ polarisation (density)
$\underset{A}{Q}{}^l = \underset{A}{\rho}(\underset{A}{v}{}^l - v^l)$ diffusion flux	$M^l = $ magnetisation (density)
$\underset{A}{q}{}^l = $ heat flux	
$\underset{A}{h}{}^l = \underset{A}{q}{}^l - \underset{A}{w}\underset{A}{Q}{}^l = $ heat flux	$\underset{A}{z} = \underset{A}{e}/\underset{A}{m} = $ specific charge
$\underset{A}{w} = \underset{A}{u} + \underset{A}{p}/\underset{A}{\rho} = $ enthalpy	$v = 1/\rho = $ specific volume

† If one admits that $B^{l(0)} \neq 0$, its value must be sufficiently small for the anisotropy of the system in its equilibrium state, induced by $B^{l(0)}$, to be negligible.

the quasineutrality requirement, E^l will always be O(1). This procedure of classification, and restriction of the basic equations so as to represent the first and second principles systematically only up to terms of O(2) leads, in the end, to a linearised form of the transport equations for dissipative quantities which describe therefore an 'infinitesimal' departure from the thermal equilibrium state.

We assume further that the total pressure tensor is symmetric, $\overset{*}{\pi}{}^{kl} = \overset{*}{\pi}{}^{lk}$, and can be expressed as a sum of reversible or recoverable pressure $p\delta^{kl}$ and an irreversible or dissipative part i.e. a viscosity tensor Π^{kl}:

$$\pi^{kl} = p\delta^{kl} + \Pi^{kl}, \qquad \Pi^{kl} = \pi\delta^{kl} + \pi^{kl}(=\Pi^{lk}), \qquad \pi = \tfrac{1}{3}\Pi^{kk}, \qquad (1.4)$$

$$\pi^{kl} = \langle \Pi^{kl} \rangle \equiv \tfrac{1}{2}(\Pi^{kl} + \Pi^{lk}) - \tfrac{1}{3}\delta^{kl}\Pi^{s3}, \qquad \pi^{kk} = 0, \qquad \overset{*}{\pi}{}^{kl} = \sum_A \overset{*}{\pi}{}_A{}^{kl}. \qquad (1.5)$$

We also assume that the polarisation and magnetisation density vectors can be represented as a sum of reversible P_0^l, M_0^l and irreversible P_+^l, M_+^l parts:

$$P^l = P_0^l + P_+^l, \qquad M^l = M_0^l + M_+^l. \qquad (1.6)$$

Both parts are considered to be O(1).

Before starting on our thermodynamic development, let us write down the conservation laws for the components and for the total system as well as the equation of motion for the material medium in their standard form, namely

$$\rho\, \mathrm{d}\underset{A}{c}/\mathrm{d}t = -\partial^l \underset{A}{Q}{}^l, \qquad \mathrm{d}\rho/\mathrm{d}t + \rho\, \partial^k v^k = 0, \qquad (\underset{A}{c} = \underset{A}{\rho}/\rho, \ \underset{A}{Q}{}^l = \underset{A}{\rho}(\underset{A}{v}{}^l - v^l)), \qquad (1.7)$$

$$\rho\, \mathrm{d}v^l/\mathrm{d}t + \partial^k \overset{*}{\pi}{}^{kl} = \rho F^l = \sum_A \underset{A}{\rho}\underset{A}{F}{}^l, \qquad \rho v^l = \sum_A \underset{A}{\rho}\underset{A}{v}{}^l, \qquad \rho = \sum_A \underset{A}{\rho}, \qquad (1.8)$$

where the ponderomotive force acting on the polarised system (see de Groot and Mazur 1962, equation (XIV, 17)) is

$$\rho F^l = \tilde{\rho}E^l + (\boldsymbol{I} \wedge \boldsymbol{B})^l + P^k\, \partial^l E^k + M^k\, \partial^l B^k + \rho\frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{\rho}[(\boldsymbol{P} \wedge \boldsymbol{B})^l - \epsilon_0\mu_0(\boldsymbol{M} \wedge \boldsymbol{E})]. \qquad (1.9)$$

2. Construction of entropy balance equation

The constitutive assumptions may be summarised in the following way. In non-stationary thermodynamics, one does not alter the first principle and we will write it for the case of a conducting fluid with polarisation (density) P^l and magnetisation (density) M^l in the form†

$$\rho\frac{\mathrm{d}u}{\mathrm{d}t} + \overset{*}{\pi}{}^{kl}\,\partial^k v^l + \partial^k q^k = J^l E''^l + \rho E''^l \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{P'^l}{\rho}\right) + \rho B''^l \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{M'^l}{\rho}\right) \qquad (2.1)$$

† The thermal energy balance equation in the form (2.1) has been given by de Groot and Mazur (1962) (equations XIV, 39) with Abraham's definition for the momentum density, $\boldsymbol{G}_{Ab} = \epsilon_0\mu_0(\boldsymbol{E} \wedge \boldsymbol{H}) = c^{-2}\boldsymbol{S}_{Ab}$. The 'Minkowskian' choice $\boldsymbol{G}_{Mi} = (\boldsymbol{D} \wedge \boldsymbol{B})$ ultimately leads to identical terms in the RHS of equation (2.1), augmented by some other terms which disappear in an approximation we will use later. However, in this second case $c^2\boldsymbol{G}_{Mi} \neq \boldsymbol{S}_{Mi} = (\boldsymbol{E} \wedge \boldsymbol{H})$, which really is not a defect, as it need not necessarily destroy the (relativistic) angular momentum balance of the whole electromechanical system taken together (cf Penfield and Haus (1967) p 241 or Møller (1952) p 205). Equation (2.1) is also used by Penfield and Haus (1967) (cf equation (4.168)) which is in reality the first law if one replaces $n\theta(\mathrm{d}/\mathrm{d}t)(s/n)$ by $-\partial^k q^k$. An equation of the type (2.1) is consistent also with equation (II.217) of de-Groot and Suttorp (1972) with slightly different terms describing the effect of magnetisation, but which may be transformed to a form identical with our equation by substituting ρu for $\rho u + M^l B''^l$.

where

$$E'^l = E^l + (v \wedge B)^l, \qquad B'^l = B^l - \epsilon_0\mu_0(v \wedge E)^l,$$
$$P'^l = P^l - \epsilon_0\mu_0(v \wedge B)^l, \qquad M'^l = M^l + (v \wedge P)^l. \tag{2.2}$$

The primed quantities may be interpreted as transforms of the unprimed ones (which are related to the local fluid co-moving frame) according to the simplified Lorentz transformation. The specific internal energy u, a standard quantity occuring in a statement of the first principle, as in conventional thermodynamics, possesses certain important distinguishing characteristics. It is a state function, that is, it is independent of the process followed in changing the state of the medium. We may say that the (specific) internal energy is a function only of chosen independent (non-dissipative) state defining variables like the specific volume $v = \rho^{-1}$, temperature T, mass fractions c_A, and the reversible part of the polarisation and magnetisation vectors P'^l_0, M'^l_0. As the equations of state for the reversible polarisation and magnetisation in isotropic media we adopt the well-known, simplest constitutive relations[†]

$$P'^l_0 = \epsilon_0\kappa_0 E'^l \qquad M'^l_0 = \frac{1}{\mu_0}\chi_0 B'^l. \tag{2.3}$$

On the other hand, in non-stationary thermodynamics, we write the second principle as

$$\rho \, ds/dt + \partial^l \mathcal{S}^l = \sigma, \qquad \sigma \geq 0 \qquad (l = 1, 2, 3), \tag{2.4}$$

which is a statement of the entropy balance equation and of the Clausius–Duhem inequality, and we have to retain explicitly all terms to order two.

Such a requirement can be satisfied by the two constitutive assumptions ((a) and (b)).

(a) The (specific) entropy s, as one of the three new quantities $(s, \mathcal{S}^l, \sigma)$ appearing in the fully independent intrinsic second principle (2.4), in a thermal non-equilibrium state, depends explicitly, not only on the usual variables $(v, c_A, u, P^l_0, M^l_0)$ for the description of reversible processes, but also on the dissipative fluxes characterising irreversible processes $(h^l_A, Q^l_A, \pi_A, \pi^{ki}_A, P^k_+, M^k_+)$, as it must also describe the irreversibility of non-equilibrium processes. Therefore

$$s = s(u_*, v, c_A, P'^l_0, M'^l_0 | Q^l_A, h^l_A, \pi_A, \pi^{kl}_A, P'^l_+, M'^l_+) \qquad (A = 1, 2, \ldots N)[‡] \tag{2.5}$$

which is different from its reversible equilibrium value

$$s_* = s(u_*, v, c_A, P'^l_0, M'^l_0 | 0, 0, \ldots). \tag{2.6}$$

According to thermodynamics the reversible (specific) entropy s_* is, for a system in equilibrium, a well-defined function of the various independent parameters (natural variables) which are necessary and sufficient to specify the thermodynamic state. For the considered multicomponent system we may choose as natural variables u, v, c_A, P'^l_0, and M'^l_0:

$$s_* = s_*(u_*, v, c_A, P'^l_0, M'^l_0). \tag{2.7}$$

[†] Detailed analysis shows that if the considered material medium is 'linear' isotropic and non-gyrotropic, and piezo-effects are neglected, then a pyro-effect would also dissappear, and we find the constitutive equations (2.3). As thermodynamics does not say anything about the functional form at state equations except that they have to satisfy certain stability conditions, equations of state must be determined either empirically or theoretically by statistical mechanics.

[‡] We consider formally P'^l and M'^l (as well as E'^l and B'^l) as a new vector field replacing P^l, M^l, E^l and B^l.

The differential equation determining the evolution of this function is the Gibbs relation, which, in the form containing a convective time derivative, stipulates the existence of local thermal equilibrium in a small moving mass element in streaming media. The Gibbs relation in the one-component system can be obtained from the first law (2.1) by the replacement $-\partial^l q^l \to \rho T \, ds_*/dt$, and by neglecting all dissipative variables, this leaves

$$\rho T \frac{ds_*}{dt} = \rho \left(\frac{du_*}{dt} + p \frac{dv}{dt} \right) - \left(E'^l \frac{dP_0'^l}{dt} + B'^l \frac{dM_0'^l}{dt} \right), \tag{2.8}$$

where we drop O(3) terms. For a multicomponent system, by a straightforward generalisation of equation (2.8) with the inclusion of additional state variables c_A characterising the mass content of components, we find

$$\rho T \frac{ds_*}{dt} = \rho \left(\frac{du_*}{dt} + p \frac{dv}{dt} \right) - \rho \sum_A \mu_A^{(0)} \frac{dc_A}{dt} - \left(E'^l \frac{dP_0'^l}{dt} + B'^l \frac{dM_0'^l}{dt} \right) \tag{2.9}$$

and thereby also the relations familiar from equilibrium theory,

$$\frac{\partial s_*}{\partial u_*} = \frac{1}{T}, \qquad \frac{\partial s_*}{\partial v} = \frac{p}{T}, \qquad \frac{\partial s_*}{\partial c_A} = -\frac{\mu_A^{(0)}}{T},$$

$$\frac{\partial s_*}{\partial P_0'^l} = -\frac{vE'^l}{T}, \qquad \frac{\partial s_*}{\partial M_0'^l} = -\frac{vB'^l}{T}, \tag{2.10}$$

by associating (and defining) the thermodynamically conjugate quantities $(T, p, \mu_A, E'^l, B'^l)$ with the original natural variables.

To find the appropriate generalised Gibbs equation valid for both reversible and irreversible changes we take the derivative of equation (2.6),

$$ds = \frac{\partial s}{\partial u_*} \, du_* + \frac{\partial s}{\partial v} \, dv + \sum_A \frac{\partial s}{\partial c_A} \, dc_A + \frac{\partial s}{\partial P_0'^l} \, dP_0'^l + \frac{\partial s}{\partial M_0'^l} \, dM_0'^l \tag{2.11}$$

$$+ \sum_A \frac{\partial s}{\partial Q_A^l} \, dQ_A^l + \sum_A \frac{\partial s}{\partial h_A^l} \, dh_A^l + \sum_A \frac{\partial s}{\partial \pi_A^{lk}} \, d\pi_A^{lk} + \sum_A \frac{\partial s}{\partial \pi_A} \, d\pi_A + \frac{\partial s}{\partial P_+'^l} \, dP_+'^l + \frac{\partial s}{\partial M_+'^l} \, dM_+'^l$$

and we also require that the dependence of s and u on the variables describing the reversible processes be the same as in reversible thermodynamics (i.e. as in equation (2.10)):

$$\frac{\partial s}{\partial u} \equiv \frac{\partial s_*}{\partial u} = \frac{1}{T}, \qquad \frac{\partial s}{\partial v} \equiv \frac{\partial s_*}{\partial v} = \frac{p}{T},$$

$$\frac{\partial s}{\partial c_A} \equiv \frac{\partial s_*}{\partial c_A} = -\frac{\mu_A^{(0)}}{T}, \qquad \frac{\partial s}{\partial P_0'^l} = -\frac{vE'^l}{T}, \qquad \frac{\partial s}{\partial M_0'^l} = -\frac{vB'^l}{T}. \tag{2.12}$$

As we are concerned with an isotropic and non-gyrotropic medium, (in the non-perturbed equilibrium state†) where dissipation effects, as a small perturbation, may

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† If one admits that $B'^{(0)} \neq 0$, its value must be sufficiently small for the anisotropy of the system in its equilibrium state, induced by $B'^{(0)}$, to be negligible.

take place, s may alternatively be expressed as a function of (isotropic) invariants of dissipative fluxes, so we can also write, instead of equation (2.5),

$$s = s(u_*, v, \underset{A}{c}, P_0'^l, M_0'^l | \underset{A}{Q'} \underset{A}{Q^l}, \underset{A}{h^l} \underset{A}{h^l}, \underset{A}{\pi^2}, \underset{A}{\pi^{kl}} \underset{A}{\pi^{kl}}, P_+'^l P_+'^l, M_+'^l M_+'^l) \qquad †(2.13)$$

Expanding s in a Taylor series about the reference state $s(u_*, v, \underset{A}{c}, P_0'^l, M_0'^l | 0, 0, \dots) \equiv s_*$, to order two in the dissipative fluxes, gives

$$s - s_* = -\frac{1}{2T} \sum_A \left(\underset{A}{G} \underset{A}{Q'} \underset{A}{Q^l} + \underset{AA}{F} \underset{A}{h^l} \underset{A}{h^l} + \underset{AA}{E} \underset{A}{\pi^{kl}} \underset{A}{\pi^{kl}} + \underset{AA}{K} \underset{A}{\pi^2} \right) - \frac{1}{2T\rho} (A P_+'^l P_+'^l + \bar{A} M_+'^l M_+'^l) \quad (2.14)$$

(where we have denoted $(\partial s/\partial \underset{A}{Q^l} \underset{A}{Q^l})_* = -(1/2T) \underset{A}{G}(u, v, \underset{A}{c})$ etc. We then find

$$\frac{\partial s}{\partial \underset{A}{Q^l}} = -\frac{1}{T} \underset{AA}{G} Q^l, \qquad \frac{\partial s}{\partial \underset{A}{h^l}} = -\frac{1}{T} \underset{AA}{F} h^l, \qquad \frac{\partial s}{\partial \underset{A}{\pi^{kl}}} = -\frac{1}{T} \underset{AA}{E} \pi^{kl},$$

$$\frac{\partial s}{\partial \underset{A}{\pi}} = -\frac{1}{T} \underset{AA}{K} \pi, \qquad \frac{\partial s}{\partial P_+'^l} = -\frac{1}{T\rho} A P_+'^l, \qquad \frac{\partial s}{\partial M_+'^l} = -\frac{1}{T\rho} \tilde{A} M_+'^l. \qquad (2.15)$$

The essence of the second principle is the statement that the entropy of an insulated system can only increase with time, i.e.

$$s - s_* \equiv s_+ \leqslant 0 \qquad (2.16)$$

for an arbitrary combination of $\underset{A}{Q^l}$, $\underset{A}{h^l}$, $\underset{A}{\pi}$, $\underset{A}{\pi^{kl}}$, $P_+'^l$ and $M_+'^l$. We may conclude therefore that since $\underset{A}{Q^l} \underset{A}{Q^l} \geqslant 0$, $\underset{A}{\pi^{kl}} \underset{A}{\pi^{kl}} \geqslant 0 \dots$)

$$\underset{A}{G} > 0, \qquad \underset{A}{F} > 0, \qquad \underset{A}{E} > 0, \qquad \underset{A}{K} > 0, \qquad A > 0, \qquad \bar{A} > 0. \qquad (2.17)$$

Making use of relations (2.11), (2.12), and (2.15) we obtain the Gibbs equation for non-stationary processes which reads

$$T\frac{ds}{dt} = \left(\frac{du_*}{dt} + p\frac{dv}{dt} \right) - \sum_A \underset{A}{\mu}^{(0)} \frac{d\underset{A}{c}}{dt} - v\left(E'^l \frac{dP_0'^l}{dt} + B'^l \frac{dM_0'^l}{dt} \right) - \sum_A \underset{AA}{G} Q^l \frac{d\underset{A}{Q^l}}{dt}$$

$$- \sum_A \underset{AA}{F} h^l \frac{d\underset{A}{h^l}}{dt} - \sum_A \underset{AA}{E} \pi^{kl} \frac{d\underset{A}{\pi^{kl}}}{dt} - \sum_A \underset{AA}{K} \pi \frac{d\underset{A}{\pi}}{dt} - v\left(A P_+'^l \frac{dP_+'^l}{dt} + \bar{A} M_+'^l \frac{dM_+'^l}{dt} \right).$$
$$(2.18)‡$$

One notices that only the two first terms on the right-hand side are of O(1) while the remaining terms are of O(2). Equation (2.18) is in several respects a generalised form of the Gibbs relation utilised in stationary irreversible thermodynamics (cf de Groot and Mazur (1962), equation (XIV 59)).

(b) The conductive part of the entropy flux $\mathscr{S}^l$ (see equation (2.5)), according to conventional irreversible thermodynamics, is proportional to only two kinds of dissipative fluxes, i.e. heat flux and diffusion fluxes, which causes $\mathscr{S}^l$ to be of O(1). Only if

† Other invariants like for example, $\underset{A}{\pi^{kl}} P^k M^l$ were not considered as being O(3).

‡ Where $\dot{s} \equiv ds/dt = \partial s/\partial t + v^l \partial^l s$. Equation (2.18) for the case $P'^l = M'^l = 0$ was derived by Kranyš (1968).

terms of O(2) are included is one able to combine all the dissipative fluxes in a vector of entropy flux. Thus a generalised definition of $\mathscr{S}^l$ may be given as $(h_A^l = q_A^l - w_A Q_A^l)$

$$
\mathscr{S}^l = \sum_A s_A^{(0)} Q_A^l - \frac{1}{T}(\beta i_+^l + \bar{\beta} y_+^l)
$$

$$
+ \frac{1}{T} \sum_A \left(h_A^l - N_A \pi_A h_A^l - M_A \pi_A^{kl} h_A^k - R_A \pi_A^{kl} Q_A^k - P_A \pi_A^{kl} i_+^k \right.
$$

$$
\left. - \bar{P}_A \pi_A^{kl} y_+^k - \gamma_A \pi_A Q_A^l - \alpha_A \pi_A i_+^l - \bar{\alpha}_A \pi_A y_+^l \right), \tag{2.19}
$$

where

$$
i_+^l = \mathrm{d}P_+^{\prime l}/\mathrm{d}t, \qquad y_+^l = \mathrm{d}M_+^{\prime l}/\mathrm{d}t \qquad \left(s_A^{(0)} T = w_A - \mu_A^{(0)} \right) \tag{2.20}
$$

are polarisation and magnetisation currents (up to O(1)) which must be involved in $\mathscr{S}^l$ rather than $P_+^{\prime l}$ and $M_+^{\prime l}$, and where $\beta, \bar{\beta}, N_A, M_A, \ldots, \bar{\alpha}_A$ are scalar coefficients which may be O(0), i.e. dependent on ρ, c_A and T only.

3. Derivation of transport equations

The new coefficients $G_A, F_A, E_A, K_A, A, \bar{A}, N_A, M_A, R_A, P_A, P_A, \gamma_A, \alpha_A, \bar{\alpha}_A, \beta$ and $\bar{\beta}$ appearing in in equations (2.18) and (2.19) and characterising the state of the medium have to conform with the phenomenological transport equations which lead to the non-negative entropy production $\sigma \geq 0$. In other words, the transport equations for dissipative fluxes can be deduced from equation (2.4) and the preceding equations by the supposition that σ is a quadratic form of the dissipative fluxes, which guarantees the condition $\sigma \geq 0$ by imposing conditions of inequality on the coefficients occurring in this quadratic form. The first law (2.1), because of equation (1.4) and $q^l = h^l + \sum_A w_A Q_A^l$, can be written as

$$
\rho(\dot{u} + p\dot{v}) + \rho\pi\dot{v} + \pi^{kl} \partial^k v^l + \partial^l h^l + \sum_A Q_A^l \partial^l w_A + \sum_A w_A \partial^l Q_A^l = J^l E^{\prime l} + i^l E^{\prime l} + y^l B^{\prime l}. \tag{3.1}
$$

Upon combining the entropy balance equation (2.4) with equations (2.18), (2.19), (1.7)$_1$, and (3.1) and retaining only terms to O(2), and using the relations

$$
\pi_A^{kl} \partial^k v^l = \pi^{kl} \langle \partial^k v^l \rangle, \qquad \pi_A^{kl} \partial^k h_A^l = \pi^{kl} \langle \partial^k h_A^l \rangle, \qquad \cdots \qquad s_A^{(0)} T = w_A - \mu_A^{(0)},
$$

$$
J^l = \sum_A z_A Q_A^l, \tag{3.2}
$$

and the 'subsidiary' condition

$$
\beta \, \partial^l i_+^l + \bar{\beta} \, \partial^l y_+^l = 0 \tag{3.3}
$$

which is satisfied, for example, in the case of absence of charge-density time variation

$$
\partial^l i_+^l = 0, \qquad \partial^l y_+^l = 0, \tag{†3.4}
$$

† This is equivalent to $\partial^l P_+^l = \tilde{\rho}_P = 0$, known as the 'transversality condition'.

one obtains

$$\sigma T = \sum_A \left(\underset{A}{Q^l} \underset{A}{U^l} + \underset{A}{h^l} \underset{A}{W^l} + \underset{A}{\pi^{kl}} \underset{A}{V^{kl}} + \underset{A}{\pi} \underset{A}{V} \right) + i_+^l X^l + y_+^l Y^l. \tag{3.5}$$

In order to reduce σT to a quadratic form one has to set

$$\underset{A}{U^l} = \sum_B \underset{AB}{C^{(Q)}} \underset{B}{Q^l}, \qquad \dots, \qquad Y^l = \bar{C} y_+^l.$$

These relations, together with an explicit form for $\underset{A}{U^l}$, $\underset{A}{W^l}, \dots$, represent just the transport equations for dissipative quantities which we are seeking:

$$\rho \underset{A}{G} \underset{A}{\dot{Q}^l} + (\partial^l w - T \, \partial^l s^{(0)}) - \underset{A}{z} E^{\prime l} + \underset{A}{R} \, \partial^k \pi^{kl} + \underset{A}{\gamma} \, \partial^l \pi = -\sum_B \underset{AB}{C^{(Q)}} \underset{B}{Q^l} = -\underset{A}{U^l}, \tag{3.6}$$

$$\rho \underset{AA}{F} \dot{h}^l + \frac{1}{T} \partial^l T + \underset{A}{N} \partial^l \pi + \underset{A}{M} \partial^k \pi^{kl} = -\sum_B \underset{AB}{C^{(h)}} \underset{B}{h^l} = -\underset{A}{W^l}, \tag{3.7}$$

$$\rho \underset{A}{E} \langle \underset{A}{\dot{\pi}^{kl}} \rangle + \langle \partial^k v^l \rangle + \underset{A}{M} \langle \partial^l h^k \rangle + \underset{A}{R} \langle \partial^l Q^k \rangle + \underset{A}{P} \langle \partial^l i_+^k \rangle + \underset{A}{\bar{P}} \langle \partial^l y_+^k \rangle = -\sum_B \underset{AB}{C^{(\bar{\pi})}} \underset{B}{\pi} = -\underset{A}{V^{kl}}, \tag{3.8}$$

$$\rho \underset{AA}{K} \dot{\pi} + \rho \dot{v} + \underset{A}{N} \partial^l h^l + \underset{A}{\gamma} \, \partial^l Q^l + \underset{A}{\alpha} \, \partial^l i_+^l + \underset{A}{\bar{\alpha}} \, \partial^l y_+^l = -\sum_B \underset{AB}{C^{(\pi)}} \underset{B}{\pi} = -\underset{A}{V}, \tag{3.9}$$

$$C i_+^l = -A P^{\prime l} - \sum_A \underset{A}{P} \partial^k \pi^{kl} - \sum_A \underset{A}{\alpha} \partial^l \pi - \left(\frac{\partial \beta}{\partial T} - \frac{\beta}{T} \right) \partial^l T - \frac{\partial \beta}{\partial v} \partial^l v + E^{\prime l} = X^l, \tag{3.10}$$

$$\bar{C} y_+^l = -\bar{A} M^{\prime l} - \sum_A \underset{A}{\bar{P}} \partial^k \pi^{kl} - \sum_A \underset{A}{\bar{\alpha}} \partial^l \pi - \left(\frac{\partial \bar{\beta}}{\partial T} - \frac{\bar{\beta}}{T} \right) \partial^l T - \frac{\partial \bar{\beta}}{\partial v} \partial^l v + B^{\prime l} = Y^l. \tag{3.11}$$

One sees that cross coupling terms, e.g. between bulk viscosity and heat flux (π, h^l) in equations (3.7) and (3.9), contain the same coefficient, namely $\underset{A}{N}$ (symbolically written $\underset{A}{N}[\pi, h^l]$). This kind of symmetry exists also for other pairs of dissipative quantities, namely

$$\underset{A}{\gamma}[\underset{A}{Q^l}, \underset{A}{\pi}], \qquad \underset{A}{R}[\underset{A}{Q^l}, \underset{A}{\pi^{kl}}], \qquad \underset{A}{N}[\underset{A}{h^l}, \underset{A}{\pi}], \qquad \underset{A}{M}[\underset{A}{h^l} \underset{A}{\pi^{kl}}],$$

$$\underset{A}{P}[\underset{A}{\pi^{kl}}, \underset{A}{i^k}], \qquad \underset{A}{\bar{P}}[\underset{A}{\pi^{kl}}, \underset{A}{y^l}], \qquad \underset{A}{\alpha}[\underset{A}{\pi}, \underset{A}{P^l}], \qquad \underset{A}{\bar{\alpha}}[\underset{A}{\pi}, \underset{A}{M^l}]. \tag{3.12}$$

However, in order to preserve the hyperbolicity of the governing equations we have to set

$$\underset{A}{P} = 0, \qquad \underset{A}{\bar{P}} = 0, \qquad \underset{A}{\alpha} = 0, \qquad \underset{A}{\bar{\alpha}} = 0, \tag{3.13}$$

as can be verified by investigation of various specialised and simplified cases of our system. This can also easily be seen if one realises that the necessary condition for the system of differential equations such as (3.6)–(3.11) to be hyperbolic is that the highest time and space derivatives in each equation have to be of the same order. This is not the case with equations (3.8) and (3.9) where, for example, the term $\alpha \, \partial^l i^l$ is in reality $\alpha \, \partial^l \, \mathrm{d}P^{\prime l}/\mathrm{d}t$, because the associate equation (3.10), according its structure, represents a

transport equation for $P^{\prime l}$ rather than for i^l. Equations (3.6)–(3.11) can be further simplified. Taking into account the Gibbs–Duhem equation to O(1) (see (A1.11)),

$$\partial^l_A p = \rho(\partial^l_A \mu^{(0)}_A + s^{(0)}_A \partial^l_A T) = \rho(\partial^l_A w_A - T \partial^l_A s^{(0)}_A) \qquad (3.14)$$

and the fact that the summation of the diffusion transport equations (3.6) multiplied by ρ_A must lead to the equation of motion of the whole material system, (1.8), one can easily see that because of (1.5) the coefficients must satisfy the relation

$$\rho \rho_A G_A = 1, \qquad \rho_A R_A = 1, \qquad \rho_A \gamma_A = 1, \qquad \sum_A \rho_A \sum_B C^{(Q)}_{AB} Q^l_B = 0. \quad (3.15)$$

Also we introduce the relaxation coefficients for polarisation and magnetisation,

$$\tau_P = C/A = \epsilon_0 \kappa_+ C, \qquad \tau_M = \bar{C}/\bar{A} = \chi_+(1/\mu_0)\bar{C}. \qquad (3.16)$$

Because of equations (3.13), (3.14), (3.15) and (3.16), equations (3.6)–(3.11) can be written as

$$\dot{Q}^l_A + \rho(\dot{v}^l_A - F^l_A) + \partial^l_A(p + \pi_A) + \partial^k_A \pi^{lk}_A = -\rho \sum_A \sum_B C^{(Q)}_{AB} Q^l_B \qquad (F^l_A = zE^{\prime l}_A), \qquad (3.17)$$

$$\dot{h}^l_A + \frac{1}{\rho F_A}\left(\frac{1}{T}\partial^l_A T + N_A \partial^l_A \pi + M_A \partial^k_A \pi^{kl}\right) = -\frac{1}{\rho F_A}\sum_B C^{(h)}_{AB} h^l_B, \qquad (3.18)$$

$$\dot{\pi}^{kl}_A + \frac{1}{\rho E_A}\left(\langle\partial^k v^l\rangle_A + M_A\langle\partial^k h^l\rangle_A + R_A\langle\partial^k Q^l\rangle_A\right) = -\frac{1}{\rho E_A}\sum_B C^{(\bar{\pi})}_{AB} \pi^{kl}_B, \qquad (3.19)$$

$$\dot{\pi}_A + \frac{1}{\rho K_A}\left(\rho\dot{v} + N_A \partial^l_A h^l + \gamma_A \partial^l_A Q^l\right) = -\frac{1}{\rho K_A}\sum_B C^{(\pi)}_{AB} \pi_B, \qquad (3.20)$$

$$\dot{P}^{\prime l}_+ - \frac{\epsilon_0\kappa_+}{\tau_P}\left[E^{\prime l} + \left(\frac{\beta}{T} - \frac{\partial\beta}{\partial T}\right)\partial^l T - \frac{\partial\beta}{\partial v}\partial^l v\right] = -\frac{1}{\tau_P}P^{\prime l}_+, \qquad (3.21)$$

$$\dot{M}^{\prime l}_+ - \frac{\chi_+}{\mu_0\tau_M}\left[B^{\prime l} + \left(\frac{\bar{\beta}}{T} - \frac{\partial\bar{\beta}}{\partial T}\right)\partial^l T - \frac{\partial\bar{\beta}}{\partial v}\partial^l v\right] = -\frac{1}{\tau_M}M^{\prime l}_+. \qquad (3.22)$$

This set of phenomenological equations we call the transport equations for our system. The right-hand side terms (in kinetic theory, these are called collision terms) represent transfer of corresponding quantities between the 'particles' of the A-component and the remaining components. Our procedure for obtaining the linearised transport equations was based on the use of the entropy balance equations which is insensible to reversible or non-thermodynamic motion (processes) inside the system. Now the diffusion equation (3.17) occupies a special position in the sense that it plays two roles: it is simultaneously an equation of motion of the A-component of the mixture and therefore a 'mechanical' equation, but, also, it is the equation of diffusional transport and therefore a 'thermodynamic' equation. This double role does not exist in a single-component system, for example. Our purely thermodynamic algorithm is not capable of predicting the mechanical non-stationary term $\rho\dot{v}^l$ in equation (3.17), but we have added it as the equation obtained by summing (3.17) over A can also be derived from equations (1.8), (1.7), (1.5), $\sum_A c_A = 1$ and $\sum_A Q^l_A = 0$. Conversely, by summation of

equation (3.17) over A, one easily obtains the overall equation of motion for the mixture (1.8).

Substituting the quantities $\underset{A}{U}{}^l$, $\underset{A}{W}{}^l$, ..., Y^l defined by equation (3.6) through (3.11) into (3.5), we find

$$\sigma T = \sum_A^N \sum_B^N \left(\underset{AB}{C}{}^{(Q)} \underset{A}{Q}{}^l \underset{B}{Q}{}^l + \underset{AB}{C}{}^{(h)} \underset{A}{h}{}^l \underset{B}{h}{}^l + \underset{AB}{C}{}^{(\bar{\pi})} \underset{A}{\pi}{}^{kl} \underset{B}{\pi}{}^{kl} + \underset{AB}{C}{}^{(\pi)} \underset{A}{\pi} \underset{B}{\pi} \right) + Ci^l_+ i^l_+ + \bar{C} y^l_+ y^l_+. \qquad (3.23)$$

To ensure the validity of the condition $\sigma T \geqslant 0$, four $(N \times N)$ matrices formed from the coefficients $\underset{AB}{C}{}^{(Q)}$, $\underset{AB}{C}{}^{(h)}$, ... and two coefficients C and $\bar{C}$ must be positive definite, which, written symbolically, reads

$$\left(\underset{AB}{C}{}^{(Q)} \right) > 0, \qquad \left(\underset{AB}{C}{}^{(h)} \right) > 0, \qquad \left(\underset{AB}{C}{}^{(\bar{\pi})} \right) > 0,$$

$$\left(\underset{AB}{C}{}^{(\pi)} \right) > 0, \qquad C > 0, \qquad \bar{C} > 0. \qquad (3.24)$$

4. Constitutive equations for polarisation and magnetisation

Relations (1.6) also lead to a resolution of the electric displacement and magnetic vectors

$$D'^l = \epsilon_0 E'^l + P'^l, \qquad H'^l = (1/\mu_0) B'^l - M'^l \qquad (4.1)$$

into reversible and irreversible parts, namely

$$D'^l = (\epsilon_0 E'^l + P'^l_0) + P'^l_+ \equiv D'^l_0 + D'^l_+,$$

$$H'^l = \left(\frac{1}{\mu_0} B'^l - M^l_0 \right) - M'^l_+ \equiv H'^l_0 + H^k_+. \qquad (4.2)$$

The standard constitutive equations for polarisation and magnetisation used for so-called 'linear media' are already described by the reversible relations (2.3)†. On the other hand, the transport equations (3.21) ((3.22)) governing the behaviour of P'^l_+ (M'^l_+), and which may include eventually the new coupling with density and temperature gradient, are well known as Debye's (1929) relaxation laws.

The generalised constitutive equations for total polarisation, for example, can be found if we write down the explicit expressions for $P'^l_0 + P'^l_+$ according to equations (2.3) and (3.21):

$$\tau_P \frac{dP'^l_+}{dt} + P'_l = \kappa \epsilon_0 E'^l + \kappa_+ \epsilon_0 \left[\left(\frac{\beta}{T} - \frac{\partial \beta}{\partial T} \right) \partial^l T - \frac{\partial \beta}{\partial v} \partial^l v \right] \qquad (\kappa = \kappa_0 + \kappa_+) \qquad (4.3)$$

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† However, it must be admitted that, generally, the reversible polarisation (and magnetisation) is not necessarily a linear function of E^l but some more general function, $P^l = f(E^l)$ say, and what we have in equation (2.3) is only the first term of a Taylor expansion about the equilibrium value of E^l (which we suppose to be zero), namely $P^l = (\partial f/\partial E^l_0)(E^l - E^l_0) + \cdots$. This is due to our linearisation procedure. Derivation of the function $f(E^l)$ would require a dynamical analysis at the microscopic level. The same applies to the other equations of state. The most one is able to do in a phenomenological theory is to introduce the (Taylor) coefficients in series expansions of such functions.

or also taking into account equation (4.12) ($P_+^l = D_+^l$),

$$\tau_{\mathrm{P}}\dot{D}_+^{\prime l} + D^{\prime l} = \epsilon\epsilon_0 E^{\prime l} + \epsilon_0 \kappa_+ \left[\left(\frac{\beta}{T} - \frac{\partial\beta}{\partial T} \right) \partial^l T - \frac{\partial\beta}{\partial v} \partial^l v \right] \qquad (\epsilon = 1 + \kappa). \tag{4.4}$$

Setting $\tau_{\mathrm{P}} = 0$ and $\beta = 0$ reduces these equations to the standard constitutive equations. Similarly to the resulting stress–strain relation (Kramyš 1977a, equation (2.25)), in equations (4.3) and (4.6) only the dissipative part of the transported quantity is relaxed. The third basic constitutive equation of electrodynamics, the generalised Ohm law, can be deduced from the transport equation (3.17) (see § 6).

Equation (4.3) for $\beta = 0$ and $P_0^{\prime l} = 0$ reduces to the form which is well known as Debye's relaxation law. Debye (1929) originally distinguished two classes of molecules: class I (non-polar molecules), containing molecules exhibiting only a weak polarisability which is due to its shape distortion (or deformation) and is independent of temperature, and class II (polar molecules), containing molecules having permanent electrical moments and exhibiting strong polarisability due to orientational effects and which is sensitive to temperature. However, Debye later accepted as more general and realistic the coexistence of both mechanisms of polarisation. There is an interesting similarity with this classification, depending on which way the condition (3.3) is fulfilled. The choice $\beta = \bar{\beta} = 0$ leads explicitly to the temperature-independent laws (3.21) and (3.22) which would describe only non-polar molecules, while a choice like (3.4) implies $\beta \neq 0$, $\bar{\beta} \neq 0$ and therefore does not eliminate the temperature dependence. Some authors (cf Debye (1929), equation (64))† simply identified orientational polarisation with $P_+^{\prime l}$ and deformation polarisation with $P_0^{\prime l}$, which we do not assume here, as we take both kinds of polarisation as partly irreversible.

5. Review of the governing equations of the theory

The transport equations, mass and momentum conservation equations and energy balance equation form the governing equations of the material (non-field) part of our system, supposing that two equations of state for u and p are given. In other words, the non-field part of the system (where E^l and B^l are considered as fixed) is completely characterised by the following $13N + 7 (= N + 1 + 3N + 3N + 5N + N + 3 + 3)$ unknown variables,

$$\rho_A (\text{or } c_A), \qquad T, \qquad v_A^l (\text{or } Q_A^l), \qquad h_A^l, \qquad \pi_A^{kl}, \qquad \pi_A, \qquad P_+^{\prime l}, \qquad M_+^{\prime l}, \qquad \ddagger(5.1)$$

which are completely determined by the non-field equations

$$(1,7)_1, \quad (3,1), \quad (3,17), \quad (3,18), \quad (3,19), \quad (3,20), \quad (3,21), \quad (3,22). \tag{5.2}$$

Defining the electric displacement D^l and magnetic vector H^l as in equation (4.1), Maxwell's equations determining electromagnetic field variations read

$$\frac{1}{\mu_0}(\nabla \wedge \boldsymbol{B})^l - \epsilon_0 \frac{\partial E^l}{\partial t} = \frac{\partial P^l}{\partial t} + (\nabla \wedge \boldsymbol{M})^l + J^l + \tilde{\rho}v^l \qquad \left(J^l = \sum_A z_A Q_A^l \right) \tag{5.3}$$

† For more on the application and derivation of Debye's relaxation formula see e.g. Van Vleck (1927), Van Vleck and Weisskopf (1945), Brown (1956).

‡ We do not need to consider $P_0^{\prime l}$ and $M_0^{\prime l}$ as unknown functions (as for example u and p) because, due to equation (2.3), both can be expressed via the field variables $E^{\prime l}$ and $B^{\prime l}$.

$$(\nabla \wedge \boldsymbol{E})^l + \partial B^l / \partial t = 0 \tag{5.4}$$

$$\epsilon_0 \partial^l E^l = -\partial^l P^l + \tilde{\rho}, \qquad \partial^l B^l = 0. \tag{5.5}$$

Equations (5.3) and (5.4) are the governing equations for the unknown variables E^l and B^l, whereas equations (5.5) are merely auxiliary equations, imposing, as they do, some limitation (or constraint) on the field (referred to as field transversality conditions if $\tilde{\rho} = 0$ as in our case); they are not true governing equations.

5.1. Summary

The quasineutral, polarisable, magnetisable charged N-component dissipative fluid mixture (assuming we use the definitions (4.1)) and the equations of state for u and p may be described by $(13N + 7)$ material variables (5.1) governed by equations (5.2), and, by six field variables E^l and B^l, which are governed by equations (5.3) and (5.4) subjected to constraints (5.5). This complete set of equations has to be solved simultaneously and may be referred to as the *electrodynamics of a quasineutral dissipative fluid*. The constitutive equations in this electrodynamics, involving the dynamics and thermodynamics of the material, are formed by $(13N + 7)$ equations generalising the well-known static constitutive material relations of electrodynamics

$$P'^l = \epsilon_0 \kappa E'^l, \qquad M'^l = \frac{1}{\mu_0} \chi B'^l, \qquad J^l = \lambda E'^l. \tag{5.6}$$

The equations (2.3), (3.21) (or (4.3)) and (3.22) generalise the first two equations of (5.6), and relation (3.17) and $J^l = \sum_{A,\,A} z_A Q_A^l$ generalise the third equation of (5.6). These correspondences are still more evident if the equations are decoupled, i.e. when viscosity and heat conduction are neglected.

5.2. Hyperbolicity.

The complete set of $(13N + 13)$ equations[†] (or $(13N + 7)$ equations if E^l and B^l are fixed), together with auxiliary conditions and the equations of state, which completely determine the behaviour of the system considered, is hyperbolic. This is evident, without direct proof, from the fact that each of the $(13N + 13)$ true governing equations contains both time and space derivatives of the same order.

If the matter and field distribution (supposing $\tilde{\rho} \neq 0$) is time-independent (i.e. we are dealing with a static system), then matter and field are governed by atemporal conservation and field equations, while transport equations describing dissipative effects are trivial, as in such a case there is no motion and therefore no dissipation, and the whole set of atemporal equations may be considered as the limiting case of a hyperbolic system describing propagation with zero velocity. However, if some motion in the system is assumed so that the dissipation process plays a role, then there must exist some non-vanishing time derivatives in the conservation equations ((1.7) (1.8) and (2.1)). If in this case we suppress time derivatives in some transport equations, in equations (3.18)–(3.20) say, then we obtain a parabolic system similar to the so called Navier–Stokes system (although in the NS case some more terms are suppressed) which results in infinite wavefront speeds. To preserve the hyperbolicity of the system, no

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[†] One of the transport equations may still be retained, as Maxwells equations contain the equation of conservation of charge.

time derivatives (or corresponding relaxation times), must be suppressed. If the (electrodynamic) constitutive equations are mutually uncoupled, then the following inequality holds for propagation mode phase speed $W < \infty$, even if the relaxation coefficients $\tau_J, \tau_P, \ldots$ are set equal to zero. This is the case when the conventional static constitutive equations are used.

5.3. Linearisation.

In this paper the local irreversible thermodynamic process is considered as a linear perturbation of the thermodynamic equilibrium state of the identical material element. In this sense the thermodynamic description given is linear, the governing equations for this process being (3.17)–(3.22) and (2.3). However, the equations describing the mechanical motion of mass, (1.7), (1.8) and (3.1), may be used in their non-linear form if so desired, at the expense of complexity and the fact that the summed-up transport equation (3.17) does not give the complete expression for the non-linear force (1.8). The second possibility is that we linearise these equations too, which will cause vanishing of the force ρF^l (equation (1.9)) as well as of the right-hand side in equation (3.1) (since we assumed, during derivation of the transport equations, $\tilde{\rho} = 0$, and E^l and B^l to be of O(1)). It should be stressed that the linearisation of the first law, (3.1), mentioned above is to be effected only after the transport equations are derived.

6. Application: two-component model

The governing equations of the N component system described are rather complex. In this section, therefore, we will limit ourselves to a tractable two-component ($N = 2$) model of a charged fluid mixture, in order to elucidate the interpretation of our new equations as well as to show some consequences of the generalised equations in some simple applications. We will assume, for the moment, formally, Case (A) of (1.3)†. Then, instead of two equations (3.17) ($A = 1, 2$) it is more convenient, for reasons of interpretation, to work with another equivalent pair of equations. The first such equation we obtain from (3.17) (or 3.6) with $F^l_{A} = z[E^l + (v \wedge B)^l]$ by the summation over the index A due to the rule (1.5)$_3$. The result is an equation of motion for the whole mixture (1.8) with ρF^l given by equation (1.9) up to terms of O(1). The condition (3.15)$_4$ means that the resulting transfer of momentum due to mutual exchanges between components cancels, and requires that

$$\rho_1\left(C^{(Q)}_{11} - C^{(Q)}_{12}\right) - \rho_2\left(C^{(Q)}_{22} - C^{(Q)}_{21}\right) = 0 \qquad \left(Q^l_2 = -Q^l_1\right). \tag{6.1}$$

Due the the relation $\sum\limits_{A}^{2} Q^l_A = 0$ we have, for the electric current.

$$J^l = zQ^l_1 + zQ^l_2 = Q^l_1(z_1 - z_2) = J^l_1(1 - z_2/z_1), \qquad J^l_2 = zQ_2^l = -(z_2/z_1)J^l_1 \tag{6.2}$$

In order to obtain the second equation, we multiply equations (3.17) by z_1 and z_2

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† We do this only in order not to lose the similarity to a typical expression although, strictly speaking, we must adhere to the supposition designated as case (B) in equation (1.3) and $\tilde{\rho} = 0$ (no limitation need be imposed on v^l).

respectively and add them together. Doing this and making use of equations (6.2), (6.1) we find

$$\frac{\mathrm{d}J^l}{\mathrm{d}t} + \tilde{\rho}\frac{\mathrm{d}v^l}{\mathrm{d}t} + \partial^k\tilde{\pi}^{lk} = -\frac{1}{\tau}J^l + \frac{\lambda}{\tau}[E^l + (v \wedge B)^l] + (\underset{1}{z} + \underset{2}{z})(J \wedge B)^l, \qquad (6.3)$$

where

$$\tilde{\pi}^{kl} = \sum_{A}^{2} \underset{A}{z}\overset{*}{\underset{A}{\pi}}^{kl}, \qquad \epsilon_0\Omega^2 = \sum_{A}^{2} \underset{A}{z}^2\underset{A}{\rho},$$

$$\frac{1}{\tau} = \rho\Big(\underset{1}{C}\overset{(Q)}{\underset{11}{}} - \underset{1}{C}\overset{(Q)}{\underset{12}{}}\Big), \qquad \lambda = \epsilon_0\Omega^2\tau \qquad (6.4)$$

mean respectively: electric dissipative pressure tensor, plasma frequency Ω, relaxation time τ and electrical conductivity λ. Equation (6.3), which is well known in the kinetic theory of a plasma (cf Spitzer (1962) equation (2.12), Lüst (1959), Greene (1973)), represents a generalisation of the static Ohm law, $J^l = \lambda E^{\prime l}$, to which it reduces if one limits consideration to stationary processes with negligible electrical viscous pressure $(\partial^k\tilde{\pi}^{kl} \simeq 0)$ and Hall current $(\tau(\underset{1}{z} + \underset{2}{z})(J \wedge B) \simeq 0)$. In a similar way instead of variables $\underset{1}{h}^l$ and $\underset{2}{h}^l$ one can use $h^l = \sum_A^2 \underset{A}{h}^l$ and $\tilde{h}^l = \sum_A^2 \underset{A}{z}\underset{A}{h}^l$ and derive from (3.7) $(A = 1, 2)$ two vector equations, one for mechanical and one for electrical quantities. The same applies to equations (3.8) and (3.9). In this way we could have one series of mechanical variables (and equations) and one series of corresponding electrical variables (and equations). Such a symmetry in our description using common quantities for temperature, polarisation and magnetisation remains incomplete.

As far as the expression for the entropy production (3.23) is concerned, we are able, because of relations (6.2), (6.1), (6.4) and (3.16), to rewrite the terms involving electrical variables (i.e. first and two last terms) in the form

$$\sigma T = \frac{\rho}{\rho_1\rho_2}\cdot\frac{\epsilon_p\Omega^2}{(z_1 - z_2)^2}\frac{1}{\lambda}J^lJ^l + \frac{\tau_P}{\epsilon_0\kappa_+}i_+^li_+^l + \frac{\tau_M\mu_0}{\chi_+}y_+^ly_+^l + \cdots. \qquad (6.5)$$

Of course only changes of $P_+^{\prime l}$ and $M_+^{\prime l}$ appear explicitly, as only these give rise to entropy production, but changes of reversible $P_0^{\prime l}$ and $M_0^{\prime l}$ do not.

7. Conclusions

A phenomenological theory for a quasineutral conducting, polarisable and magnetisable N-component dissipative fluid mixture whose equations form a hyperbolic system is proposed. These equations are similar in many respects to Grads' approximation of the kinetic theory of a plasma (cf Kranyš and Teichmann (1974)), but they describe, in addition, the particles internal degrees of freedom (associated with polarisation and magnetisation) and also bulk viscosity effects which kinetic theory is hardly able to describe. The non-stationary transport equations for dissipative fluxes containing new cross-effect terms and possessing certain symmetries, as required for compatibility with the entropy principle expressed by the new balance equation (including a new Gibbs equation) including second-order terms, have been deduced in order to guarantee physical causality and the possibility of describing fast transient processes. The theory formed by the set of $(13N + 7)$ partial differential equations (with some auxiliary

equations) governing the material behaviour of the system, generalising the constitutive equations (5.6), together with six field-governing Maxwell's equations (with two auxiliary conditions) may be referred to as phenomenological electrodynamics of dissipative quasineutral fluid media. It is shown how the new transport equations for P'^l, M'^l and $\underset{A}{Q}'^l$ reduce, under special conditions, to the well-known polarisability formulae, Debye's laws and Ohm's law respectively. In many cases the simple Debye formula for the susceptibility (uncoupled from thermodynamics) failed to fit the data satisfactorily and therefore attempts were made to improve it in different ways (cf Brown (1956) § 65). These attempts seem to us to be rather a computational patch-work. Apart from this, Debye's and Lorentz's formulae for susceptibility were unified at the level of Boltzmann statistics by Van Vleck and Weisskopf (1945) (= revised Lorentz's theory) in the sense that the effect of collisions (i.e. dissipation) gives a compatible dispersion and absorption in both the resonant (Lorentz) and non-resonant (Debye) cases.

Our new equations describing a polarisation dynamics show a relaxation similar to a simple Debye law (in which relaxation is supposed to be due to rotational friction only) and, besides that, also the dependence on temperature and density gradients. Presumably, the dissipative effects are formally more completely described by our theory (based on non-stationary thermodynamics) than in the revised Lorentz or Debye theory, while for the reversible effects of polarisation the statistical approach of a revised Lorentz theory allows to give a detailed (microscopic) description of susceptibility which is beyond the scope of the thermodynamic approach. The corrections to the susceptibility formulae are expected to be experimentally observed, especially in the microwave region.

From the thermodynamic functions involved in the first and second principles the remaining thermodynamic functions in the non-stationary version are established too. (See appendix 1.)

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Appendix 1: Other thermodynamical functions in non-stationary theory

Relations between overall and partial specific quantities for entropy, internal energy, free energy, and pressure are

$$s = \sum_A \underset{A}{c}\,\underset{A}{s}, \qquad u = \sum_A \underset{A}{c}\,\underset{A}{u}, \qquad f = \sum_A \underset{A}{c}\,\underset{A}{f}, \qquad pv = \sum_A \underset{A}{c}\,\underset{A}{p}/\underset{A}{\rho}, \quad \text{(A1.1)}$$

where $\underset{A}{c} = \underset{A}{\rho}/\rho$ and $\sum_A \underset{A}{c} = 1$. By integration of the general Gibbs equation (2.18), keeping constant all reversible natural variables u (or T), v, $\underset{A}{c}$, P_0^l and M_0^l, one finds easily the same result as would follow directly from (2.16) and (2.14) i.e. $s = s_* + s_+$ or,

written for each specific partial entropy, and using equation (A1.1)

$$\underset{A}{s_+} \equiv \underset{A}{s} - \underset{A}{s_*} = -\frac{1}{2T}\left[\frac{1}{\underset{A}{c}}\left(\underset{A}{G}\underset{A}{Q^l}\underset{A}{Q^l} + \cdots + \underset{A}{K}\underset{A}{\pi}\underset{A}{\pi}\right) + v\left(\underset{A}{A}P_+^{ll}P_+^{ll} + \underset{A}{\bar{A}}M_+^{ll}M_+^{ll}\right)\right].\qquad (A1.2)$$

In reversible thermodynamics one introduces the free energy f_* and Gibbs function G_*:

$$f_* = u_* - Ts_*, \qquad G_* = u_* + pv - Ts_*, \qquad (A1.3)$$

where only quantities characterising reversible changes are involved. These definitions and even the complete Gibbs equation are formally taken over, and supposed to be valid also in traditional non-equilibrium thermodynamics which is stationary, since it neglects, among other things, the inertial effects of dissipative fluxes. This cannot be done at the level of our non-stationary theory, as is evident from relation (A1.2). We may generatize relations (A1.3) by defining the free energy f and Gibbs function G in terms of quantities characterising general (not only reversible) changes:

$$f \equiv u - Ts = f_* + f_+; \qquad f_+ \equiv u_+ - Ts_+, \qquad (A1.4)$$

$$G \equiv u + (p + \pi)v - Ts = G_* + G_+; \qquad G_+ \equiv u_+ + \pi v - Ts_+, \qquad (A1.5)$$

where f_* and G_* are defined by (A1.3), $u = u_* + u_+$ and where s_+ is given by equation (2.16). For example, from equations (A1.5) and (A1.1) we find

$$G \equiv \sum_A \underset{A}{c}\underset{A}{\mu} = \sum_A \underset{A}{c}\left(\underset{A}{u} + p_A + \underset{A}{\pi}\right)/\rho - T\underset{A}{s}\right), \qquad (A1.6)$$

and structure also the generalised chemical potentials

$$\underset{A}{\mu} = \underset{A}{u} + (p + \underset{A}{\pi})/\rho - T\underset{A}{s} = (\underset{A}{\mu_*} - T\underset{A}{s_*}) + \left(\underset{A}{\mu_+} + \frac{\pi}{\rho} - T\underset{A}{s_+}\right) \equiv \underset{A}{\mu_*} + \underset{A}{\mu_+}, \quad (A1.7)$$

where $\underset{A}{s_+}$ is given by equation (A1.2) and where

$$\underset{A}{\mu_*} = \underset{A}{\mu^{(0)}} + \underset{A}{\mu^{(1)}}, \qquad (A1.8)$$

$$\underset{A}{\mu^{(0)}} = \underset{A}{u^{(0)}} + \underset{A}{p^{(0)}}/\rho - T\underset{A}{s^{(0)}}, \qquad \underset{A}{\mu^{(1)}} = \underset{A}{\mu^{(1)}}(P_0^{ll}, M_0^{ll}, \ldots). \qquad (A1.9)$$

$\underset{A}{\mu^{(0)}}$ is the reversible polarisation independent part of the chemical potential which is entirely O(0), while $\underset{A}{\mu^{(1)}}$ is dependent on polarisation contributions or field. In equation (A1.7) $\underset{A}{\mu} - \underset{A}{\mu_*} = \underset{A}{\mu_+}$ is O(2) (as well as $\underset{A}{\mu} - \underset{A}{\mu^{(0)}}$). This is the reason why formulae (2.18) or (2.19), where only O(2) terms are included, cannot involve the non-stationary corrections $\underset{A}{s_+}$ or $\underset{A}{\mu_+}$. (Only the first non-stationary term in (A1.7) is known (cf de Groot and Mazur (1962) equation III, 37).)

We can easily find also the non-stationary Gibbs–Duhem equation. Differentiating the defining relation (A1.5) and substituting for $du + p\, dv - T\, ds$ the expression which follows from the Gibbs equation (2.18) (keeping terms up to O(2) only) we obtain

$$\sum_A \underset{A}{c}\, d\underset{A}{\mu} = v\,(dp + d\pi) - s^{(0)}\, dT + v(E''\, dP_0^{ll} + B''\, dM_0^{ll}) + v(AP_+^{ll}\, dP_+^{ll} + \bar{A}M_+^{ll}\, dM_+^{ll})$$

$$\qquad\qquad\qquad (A1.10)$$

$$+ \pi\, dv + du_+ + \sum_A \left(\underset{A}{G}\underset{A}{Q^l}\, d\underset{A}{Q^l} + \underset{A}{F}h^l\, d\underset{A}{h^l} + \cdots + \underset{A}{K}\underset{A}{\pi}\, d\underset{A}{\pi}\right).$$

or

$$d\mu_A = d(p_A + \pi_A)/\rho_A - s_A^{(0)}\, dT + \pi_A\, dv + du_+ + (G/c)Q^l_A\, dQ^l_A + \cdots$$

$$+ v(E'^l\, dP_0'^l + AP_+'^l\, dP_+'^l) + \cdots \tag{A1.11}$$

which is compatible with (A1.7) within O(2) terms $\left(d\mu_A^{(0)} = dp_A/\rho_A - s_A^{(0)}\, dT\right)$.

Appendix 2: Illustrative example

In the following illustrative example we want to show how non-stationary thermodynamics, which is especially well suited to rapidly time varying electromagnetic phenomena, might be incorporated in a description of microwaves or even optical range waves in dissipative media. Let us take a two-fluid model without viscosity, heat conduction and magnetisation (i.e. $\pi_A^{kl} = \pi_A = h_A^l = M^l = 0$, $\beta = $ constant). Suppose that v^l, B^l, E^l and P^l disappear at equilibrium, i.e. are O(1). The completely linearised system, where only the terms up to O(1) are considered in the material governing equations ((1.7), (1.8), (3.1), (6.3) and (3.21)), reads

$$\frac{\partial p}{\partial t} + \partial^l v^l = 0, \qquad \rho\frac{\partial v^l}{\partial t} + \partial^l p = 0, \qquad \rho\left(\frac{\partial u}{\partial t} + p\frac{\partial v}{\partial t}\right) = 0, \tag{A2.1}$$

$$\partial^l J^l = 0, \qquad \tau_J\frac{\partial J^l}{\partial t} + J^l - \lambda E^l = -\partial^l \tilde{p}, \qquad \tau_P\frac{\partial P_+^l}{\partial t} + P_+^l - \epsilon_0\kappa E^l = \epsilon_0\kappa\frac{\beta}{T}\partial^l T. \tag{A2.2}$$

On the other hand, we deduce, from Maxwell's equations (5.3) to (5.5) subject to conditions $\partial^l P^l = 0$ (cf equation (3.4)) $P_0^l = \epsilon_0\kappa_0 E^l$ (cf equations (2.3) and (1.6)) and $\tilde{\rho} = 0$

$$\left(\partial^s\partial^s - \epsilon_0\mu_0(1 + \kappa_0)\frac{\partial^2}{\partial t^2}\right)E^k - \mu_0\frac{\partial^2}{\partial t^2}P_+^k - \mu_0\frac{\partial J^k}{\partial t} = 0. \tag{A2.3}$$

As equations (A2.1) contain no electrical variables like J^l, P_+^l or E^l, they can be solved separately (if appropriate state equations are given) and the same applies to the remaining electrodynamic equations (A2.2) and (A2.3) where terms containing $\partial^l\tilde{\rho}$ and $\partial^l T$ have to be considered as *a* given driving source determined by the mechanical equations. The solution of equations (A2.1) represents the well-known adiabatic acoustical wave accompanying the damped electromagnetic wave, whose propopagation mode can be found by the standard techniques for plane wave propagation. Such an approximation is close to the standard approximation utilised in optics, where the mechanical and thermodynamic processes accompanying an electrical wave are completely neglected. However, in the general case, the cross-effect terms will prevent the separation of the mechanical problem from the electrodynamic problem and will involve the whole thermodynamics in a consideration of electromagnetic phenomena in dissipative matter.

Note added in proof. In the light of the author's recent studies, the present formulation can be improved in the following way.

(1) Instead of internal energy $u(= u_1)$ defined by the first law, expressed by equation (2.1), as a function of independent variables (T, v, P'^l, M'^l) it is more convenient to choose another definition, namely

$$u_2 = u_1 - v(P'^l E'^l + M'^l B'^l) \qquad \text{and} \qquad du_2 = du_1 - v(E'^l dP'^l + P'^l dE'^l + \ldots). \tag{A3.1}$$

Equation (2.1) then reads $\rho \dot{u}_2 + \ldots = \ldots - (P''\dot{E}'^l + M''\dot{B}'^l)$. This Legendre transformation (A3.1) results in exchanging state variables (P'^l, M'^l) for (E'^l, B'^l). So $u_2 = u_2(T, v, E'^l, B'^l)$.

(2) We need to know the explicit dependence of the u on the electromagnetic quantities, which is

$$u_{1,2} = \bar{u}(v, T) \pm \tfrac{1}{2}v(P'^l E'^l + M'^l B'^l) \equiv u_{1,2*} + u_{1,2+}. \tag{A3.2}$$

Recalling (1.6), we have also

$$u_{1,2*} = \bar{u} \pm \tfrac{1}{2}v(P_0'^l E'^l + M_0'^l B'^l); \qquad u_{1,2+} = \pm \tfrac{1}{2}v(P_+'^l E'^l + M_+'^l B'^l), \qquad \mathrm{d}u_{1,2+}/\mathrm{d}t = \pm \tfrac{1}{2}v(P_+'^l \dot{E}'^l + M_+'^l \dot{B}'^l). \tag{A3.3}$$

This cannot be obtained from (2.1) but from the energy balance equation showing explicitly all electromagnetic terms (see Krany's (1979) equation (3.13)).

(3) In $\mathscr{S}^l$, as given by (2.20), it is necessary to replace i_+^l and y_+^l by the $P_+'^l$ and $M_+'^l$ respectively.

(4) Since in (2.14) there is the sum of three separate invariant terms involving polar vectors h_A^l, $P_+'^l$ and Q_A^l, a more general unified invariant expression can be constructed from them. The same applies in forming the invariant expression (3.23).

(5) If one limits the form of the constitutive relations $P_0'^l = P_0'^l(T, v, E'^k, B'^k)$, $M_0'^l = M_0'^l(T, v, E'^k, B'^k)$ only to (2.3) the pyro-, piezo-electric and gyrotropic effects are excluded.

Taking into account the points (1), (2), (3) and (5), we can derive transport equations similar to (3.6)–(3.11). Equations (3.6) and (3.7) remain unchanged, in (3.8) and (3.9) one has to replace i_+^l and y_+^l by $P_+'^l$ and $M_+'^l$, while (3.10) takes the form

$$\tau_P \frac{\mathrm{d}P_+'^l}{\mathrm{d}t} + P'^l = -\tau_P 2\kappa_+ \epsilon_0 \left(\frac{1}{2} \frac{\mathrm{d}E'^l}{\mathrm{d}t} + \sum_A P_A^0 \partial^l \pi_A^{kl} + \sum_A \alpha_A \partial^l \pi_A + \partial^l \beta - \frac{\beta}{T} \partial^l T \right), \tag{A3.4}$$

where $2\kappa_+ \epsilon_0 = A^{-1}$, $\tau_P = A . C^{-1}$, and similarly for equation (3.11). One notices that the leading term $\tfrac{1}{2}\dot{E}'^l$ has its origin in $\dot{u}_{2+}$. In contrast to the transport equations (3.6)–(3.11) the new system is hyperbolic without additional requirements like (3.13), and shows the coupling of shear and bulk viscosity with polarisation and magnetisation. The Debye law as given by (A3.4) (as well as the definition of u_2 (A3.2)) is in conformity to that given by Dixon (1978) p 238, which contains also the coupling term with heat flux. Such a term we can obtain as well, if point (4) is respected. This, together with the formulae for general linear constitutive equations for $P_0'^l$ and $M_0'^l$ free of the limitation mentioned in point (5), are given in the author's 'Relativistic electrodynamics' (*Can. J. Phys.* submitted for publication).

For completeness we given the list of replacements in the formulae resulting from the changes specified in points (1), (2), and (3).

In equations

(2.1) and (3.1):	$\dot{u} \to \dot{u}_2,$ $\quad E\dot{P} + B\dot{M} \to -(P\dot{E} + M\dot{B});$

| (2.5)–(2.7) and (2.13): | $u_* \to u_{2*},$ $\quad P_0 \to E, \quad M_0 \to B;$ |

| (2.8), (2.9) and (2.18): | $s_* \to s_{2*}, \quad u_* \to u_{2*}, \quad -(E\dot{P}_0 + B\dot{M}_0) \to (P_0\dot{E} + M_0\dot{B}), \quad s \to s_2;$ |

| (2.10) and (2.12): | $s_* \to s_{2*}, \quad P_0 \to E, \quad E \to -P_0, \quad M_0 \to B, \quad B \to -M_0;$ |

| (2.11): | $u_* \to u_{2*}, \quad P_0 \to E, \quad M_0 \to B;$ |

(2.19), (3.3)–(3.5),
(3.8)–(3.11), (3.23), (6.5): $i_+ \to P_+, \qquad y_+ \to M_+;$

(3.10) and (3.11): $E \to -\tfrac{1}{2}\dot{E}, \quad P_+ \to \dot{P}_+, \quad B \to -\tfrac{1}{2}\dot{B}, \quad M_+ \to \dot{M}_+;$

(3.16) reads: $\tau_P = AC^{-1} = (2\epsilon_0 \kappa_+ C)^{-1}, \qquad \tau_M = \bar{A}\bar{C}^{-1} = u_0(2\kappa_+ \bar{C})^{-1};$

(6.5): $\tau_P \to (2\tau_P)^{-1}, \qquad \tau_M \to (2\tau_M)^{-1};$

(A1.10) and (A1.11): $u_* \to u_{2*}, \quad (e\mathrm{d}P_0 + B\mathrm{d}M_0) \to -(P_0\mathrm{d}E + M_0\mathrm{d}B).$

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