Statistical description
of field and matter

1 Macroscopic laws

The electromagnetic and material quantities that occur in the atomic equations show rapid changes in space and time. To describe macroscopic situations one has to find laws which contain physical quantities that change much slower in space and time. The reason is that such quantities are measured by means of macroscopic devices. These instruments do not yield information on individual particles, but averages over large numbers of particles contained in domains which are small compared to the total system.

So, if one wants to derive the macroscopic laws from the atomic equations some averaging procedure must be used. To that purpose one must define macroscopic quantities as statistical averages over a number of atoms contained in a mass element which is large enough so that the principles of statistical mechanics may be applied, but which is still small from a macroscopic point of view. As is implied by the definition of the macroscopic quantities the spatial dimensions of the mass elements should be on the one hand large compared to the distance between neighbouring atoms and on the other hand small compared to macroscopic distances. The possibility to realize such a situation requires the system to fulfil suitable physical conditions. Gases, liquids and solids will satisfy these conditions under wide ranges of physical circumstances. In gases the density should not be so small that the dimension of the mass cell would have to be excessive in order to fulfil the condition that the cell must contain many atoms.

The macroscopic quantities are thus rid of the extremely rapid changes in space and time which the corresponding microscopic quantities show. In fact, just as in the rest of macroscopic physics, the physical quantities can then be considered as continuous functions of the space-time coordinates, except at boundaries.

After having indicated how such macroscopic quantities may be described with the help of distribution functions, we shall derive in this chapter the

macroscopic equations that govern the behaviour of fields and matter in bulk: the Maxwell equations, the momentum, energy and angular momentum balances and the laws of thermodynamics, all in the framework of classical non-relativistic theory.

2 Average quantities

Formally one may represent statistical averages with the help of distribution functions. In the non-relativistic approximation all dynamical quantities depend only on the positions R_{ki} and velocities $\dot{R}_{ki}$ of the particles ki. Thus the averages of a microscopic quantity $a(R_{ki}, \dot{R}_{ki}, t)$ can be considered as an average in a 'fluxion' space spanned by the positions and velocities of the particles:

$$A(R, t) = \langle a \rangle = \int a f \, d\varphi, \tag{1}$$

where $f = f(R_{ki}, \dot{R}_{ki}; t)$ depends on the particle positions R_{ki} and velocities $\dot{R}_{ki}$ and where $d\varphi = \prod_{ki} dR_{ki} d\dot{R}_{ki}$ is the fluxion space element. The probability to find the system in the volume element $d\varphi$ is $f d\varphi$.

Now from the conservation of probability one may conclude that time differentiation and averaging of a quantity commute. This is seen in the following way. The probability to find the system in the fluxion space element $d\varphi$ is given by $f d\varphi$. This measure $f d\varphi$ remains constant in time if one follows the region of fluxion space points in their natural motion in fluxion space. Therefore one has:

$$\frac{\partial}{\partial t} \langle a \rangle \equiv \frac{\partial}{\partial t} \int a f \, d\varphi = \int \frac{da}{dt} f \, d\varphi \equiv \left\langle \frac{da}{dt} \right\rangle, \tag{2}$$

where d/dt is the total time derivative in fluxion space $\partial/\partial t + \sum_{ki} \dot{R}_{ki} \cdot V_{ki} + \sum_{ki} \ddot{R}_{ki} \cdot V_{ki}^{\cdot}$ (where $V_{ki}^{\cdot} \equiv \partial/\partial \dot{R}_{ki}$ and where $\ddot{R}_{ki}$, as a consequence of the equations of motion, depends on all R_{lj} and $\dot{R}_{lj}$ and on time). Equation (2) shows that time differentiation and averaging commute.

Space differentiation and averaging commute trivially:

$$\nabla \langle a \rangle = \langle \nabla a \rangle, \tag{3}$$

because the fluxion space distribution function does not depend on the space coordinates.

Often the quantities a are sums of functions which depend on the variables pertinent to one atom or to two atoms only. In such cases one may perform

a number of integrations in the expression (1) for the average A. For instance, if $a = \sum_k a_k(R_{ki}, \dot{R}_{ki})$ (where R_{ki} stands for $R_{k1}, R_{k2}, ...$) or alternatively, with mass centre and internal coordinates and velocities, $a = \sum_k a_k(R_k, \dot{R}_k, r_{ki}, \dot{r}_{ki})$ one may write the average A in terms of a 'one-point distribution function' $f_1(R_1, \dot{R}_1, r_{1i}, \dot{r}_{1i}; t)$ as

$$A = \int a_1(R_1, \dot{R}_1, r_{1i}, \dot{r}_{1i}) f_1(R_1, \dot{R}_1, r_{1i}, \dot{r}_{1i}; t) dR_1 \, d\dot{R}_1 \prod_i dr_{1i} d\dot{r}_{1i}, \tag{4}$$

or, in a shorter notation,

$$A = \int a_1(1) f_1(1; t) d1, \tag{5}$$

where $f_1(1; t) d1$ is the probability, normalized to N (the number of atoms in the system), to find an atom with parameters in the range $dR_1 \, d\dot{R}_1 \prod_i dr_{1i} d\dot{r}_{1i}$ around the point $R_1, \dot{R}_1, r_{1i}, \dot{r}_{1i}$ ($i = 1, 2, ...$) in fluxion space.

Likewise, if a has the form $a = \sum_{k, l(k \neq l)} a_{kl}(k, l)$, one may write

$$A = \int a_{12}(1, 2) f_2(1, 2; t) d1 \, d2, \tag{6}$$

where $f_2(1, 2; t) d1 \, d2$ is the joint probability, normalized to $N(N-1)$, to find one atom in the range d1 and another in the range d2.

It will be convenient to introduce also a two-point correlation function defined as

$$c_2(1, 2; t) \equiv f_2(1, 2; t) - f_1(1; t) f_1(2; t). \tag{7}$$

This correlation function has the property to vanish rapidly with increasing atomic distances for systems without long range order, such as fluids. For crystals however this is not the case.

In the preceding the treatment was confined to one-component systems. The extension to mixtures of several components is straightforward. In that case one has to introduce distribution functions for each separate species. The one-point distribution function $f_1^a(1; t)$ now gets an extra label a which indicates the species. Now $f_1^a(1; t) d1$ is the probability, normalized to N^a (the number of atoms of species a), to find an atom of species a with parameters in the range d1 in fluxion space. Similarly the two-point distribution function is defined in such way that $f_2^{ab}(1, 2; t) d1 \, d2$ is the joint probability, normalized to $N^a N^b$ (if $a \neq b$) or $N^a(N^a - 1)$ (if $a = b$), to find an atom of species a in the range d1 and an atom of species b in the range d2. The correlation function $c_2^{ab}(1, 2; t)$ is now defined as the difference $f_2^{ab}(1, 2; t) - f_1^a(1; t) f_1^b(2; t)$.

3 The Maxwell equations

The Maxwell equations may be found from the atomic field equations (I.35) by the statistical procedure of the preceding section. Indeed one gets:

$$\langle \mathbf{V} \cdot \mathbf{e} \rangle = \langle \rho^e \rangle - \langle \mathbf{V} \cdot \mathbf{p} \rangle,$$

$$-\langle \partial_0 \mathbf{e} \rangle + \langle \mathbf{V} \wedge \mathbf{b} \rangle = \langle \mathbf{j} \rangle / c + \langle \partial_0 \mathbf{p} \rangle + \langle \mathbf{V} \wedge \mathbf{m} \rangle,$$

$$\langle \mathbf{V} \cdot \mathbf{b} \rangle = 0,$$

$$\langle \partial_0 \mathbf{b} \rangle + \langle \mathbf{V} \wedge \mathbf{e} \rangle = 0. \tag{8}$$

With the help of the commutation rules (2) and (3) one obtains from (8) the set of equations

$$\mathbf{V} \cdot \langle \mathbf{e} \rangle = \langle \rho^e \rangle - \mathbf{V} \cdot \langle \mathbf{p} \rangle,$$

$$-\partial_0 \langle \mathbf{e} \rangle + \mathbf{V} \wedge \langle \mathbf{b} \rangle = \langle \mathbf{j} \rangle / c + \partial_0 \langle \mathbf{p} \rangle + \mathbf{V} \wedge \langle \mathbf{m} \rangle,$$

$$\mathbf{V} \cdot \langle \mathbf{b} \rangle = 0,$$

$$\partial_0 \langle \mathbf{b} \rangle + \mathbf{V} \wedge \langle \mathbf{e} \rangle = 0. \tag{9}$$

With the notations (1) for the macroscopic quantities, i.e. macroscopic fields

$$\mathbf{E} = \langle \mathbf{e} \rangle, \qquad \mathbf{B} = \langle \mathbf{b} \rangle, \tag{10}$$

the macroscopic charge and current densities

$$\varrho^e = \langle \rho^e \rangle, \qquad \mathbf{J} = \langle \mathbf{j} \rangle, \tag{11}$$

and the macroscopic polarization vectors

$$\mathbf{P} = \langle \mathbf{p} \rangle, \qquad \mathbf{M} = \langle \mathbf{m} \rangle, \tag{12}$$

one may write for the set (9):

$$\mathbf{V} \cdot \mathbf{E} = \varrho^e - \mathbf{V} \cdot \mathbf{P},$$

$$-\partial_0 \mathbf{E} + \mathbf{V} \wedge \mathbf{B} = \mathbf{J} / c + \partial_0 \mathbf{P} + \mathbf{V} \wedge \mathbf{M},$$

$$\mathbf{V} \cdot \mathbf{B} = 0,$$

$$\partial_0 \mathbf{B} + \mathbf{V} \wedge \mathbf{E} = 0. \tag{13}$$

These are the *Maxwell equations*. With the definitions of the displacement vectors

$$\mathbf{D} = \mathbf{E} + \mathbf{P}, \qquad \mathbf{H} = \mathbf{B} - \mathbf{M}, \tag{14}$$

they may be written alternatively as

$$\mathbf{V} \cdot \mathbf{D} = \varrho^e,$$

$$-\partial_0 \mathbf{D} + \mathbf{V} \wedge \mathbf{H} = \mathbf{J} / c,$$

$$\mathbf{V} \cdot \mathbf{B} = 0,$$

$$\partial_0 \mathbf{B} + \mathbf{V} \wedge \mathbf{E} = 0. \tag{15}$$

The latter could also have been obtained by averaging the atomic equations (I.37).

Maxwell's equations have thus been found from the atomic field equations, which in turn followed from Lorentz's microscopic field equations. This completes the derivation.

The macroscopic equation of conservation of charge

$$\partial \varrho^e / \partial t = -\mathbf{V} \cdot \mathbf{J} \tag{16}$$

follows from the averaging of (I.38) with the help of the definitions (11) and the fact that averaging and differentiation commute.

Up to order c^{-1} the solutions of the Maxwell equations (13) are

$$\mathbf{E}(\mathbf{R}, t) = \mathbf{E}_e(\mathbf{R}, t) - \mathbf{V} \int \{ \varrho^e(\mathbf{R}', t) - \mathbf{V}' \cdot \mathbf{P}(\mathbf{R}', t) \} \frac{1}{4\pi |\mathbf{R} - \mathbf{R}'|} \, \mathrm{d}\mathbf{R}',$$

$$\mathbf{B}(\mathbf{R}, t) = \mathbf{B}_e(\mathbf{R}, t)$$

$$+ \mathbf{V} \wedge \int \left\{ c^{-1} \mathbf{J}(\mathbf{R}', t) + c^{-1} \frac{\partial \mathbf{P}(\mathbf{R}', t)}{\partial t} + \mathbf{V}' \wedge \mathbf{M}(\mathbf{R}', t) \right\} \frac{1}{4\pi |\mathbf{R} - \mathbf{R}'|} \, \mathrm{d}\mathbf{R}'. \tag{17}$$

One may verify that these are the solutions of (13) by inserting them and using (16) (v. problem 1). The first terms at the right-hand sides are the external fields, which are solutions of the field equations without sources.

The macroscopic charge and current densities ϱ^e and $\mathbf{J}$ are the averages (11) of (I.33)

$$\varrho^e(\mathbf{R}, t) = \langle \rho^e \rangle = \langle \sum_k e_k \delta(\mathbf{R}_k - \mathbf{R}) \rangle,$$

$$\mathbf{J}(\mathbf{R}, t) = \langle \mathbf{j} \rangle = \langle \sum_k e_k \mathbf{v}_k \delta(\mathbf{R}_k - \mathbf{R}) \rangle, \tag{18}$$

or, in terms of one-point distribution functions, as in (4):

$$\varrho^e(\mathbf{R}, t) = \sum_a e_a f_1^a(\mathbf{R}; t),$$

$$\mathbf{J}(\mathbf{R}, t) = \sum_a \int e_a \mathbf{v}_1 f_1^a(\mathbf{R}, \mathbf{v}_1; t) \mathrm{d}\mathbf{v}_1, \tag{19}$$

where the summation over a is extended over the number of species in the system. These expressions include contributions from all charged 'atoms', such as ions and free conduction electrons.

Furthermore the macroscopic electric and magnetic polarizations are given by the averages (12) of (I.34):

$$P(R, t) = \langle p \rangle = \left\langle \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \sum_k \overline{\mu}_k^{(n)} \delta(R_k - R) \right\rangle,$$

$$M(R, t) = \langle m \rangle = \left\langle \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \sum_k (\overline{\nu}_k^{(n)} + c^{-1} \overline{\mu}_k^{(n)} \wedge v_k) \delta(R_k - R) \right\rangle, \tag{20}$$

or in terms of one-point distribution functions:

$$P(R, t) = \sum_a \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \int \overline{\mu}_1^{(n)} f_1^a(R, 1; t) d1,$$

$$M(R, t) = \sum_a \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \int (\overline{\nu}_1^{(n)} + \overline{\mu}_1^{(n)} \wedge \beta_1) f_1^a(R, 1; t) d1, \tag{21}$$

where the symbol 1 now indicates all atomic parameters except for the position i.e. $\overline{\mu}_1^{(n)}$ in the first line and $\overline{\mu}_1^{(n)}$, $\overline{\nu}_1^{(n)}$ and $\beta_1 \equiv v_1/c$ in the second line. Just as the multipole moments may be permanent or induced or both, the polarization vectors P and M are the total polarizations, due to permanent or induced effects or both.

The quantities (18–21) are continuous functions of space and time coordinates; they contain the charge e_k and the multipole moments $\overline{\mu}_k^{(n)}$ and $\overline{\nu}_k^{(n)}$ as atomic characteristics.

A few remarks may be made on the result. In the first place it is seen to be valid for completely arbitrary polarizations of the material, that is to say polarizations due to both permanent and induced (by means of external and internal fields) electromagnetic moments of the atoms. The derivation leads to polarization vectors P and M expressed in (20) and (21) as statistical averages involving the electromagnetic moments of the atoms. The derivation is therefore completely independent of the 'constitutive relations', by which connexions between the polarizations and the fields are given, usually in terms of electric and magnetic susceptibilities. In fact these connexions belong to the dynamics (or statics) of the system, not to its set of field equations.

In the second place the derivation shows the secondary character of the displacement vectors D and H. They may be obtained from their definitions (14) together with (10) and (12) for the fields and polarizations. The set (15) is useful to formulate the boundary conditions which lead to the well-known

operational definitions of the Maxwell fields E, B, D and H in certain cavities. But otherwise the set (13) is to be preferred since it shows better the microscopic origin of the equations, as is apparent from the derivation.

The field equations (13) may be shown to be covariant under Galilei transformations. These form a group consisting of spatial rotations and pure Galilei transformations. The latter have the form

$$R' = R + Vt,$$
$$t' = t, \tag{22}$$

where V is the transformation velocity (independent of space and time). The covariance of the field equations under rotations is guaranteed by the fact that they have been written in vector notation. The covariance under pure Galilean transformations requires some further inspection. From (22) we have for the transformations of the partial derivations with respect to space and time

$$\nabla' = \nabla,$$
$$\frac{\partial}{\partial t'} = \frac{\partial}{\partial t} - V \cdot \nabla. \tag{23}$$

Furthermore the distribution functions are invariant:

$$f_1^{a'}(1'; t') = f_1^a(1, t), \tag{24}$$

as a consequence of their probability interpretation. Here $1'$ denotes the transformed quantities of the atom 1, for instance $R_1' = R_1 + Vt$, $v_1' = v_1 + V$, $\overline{\mu}_1' = \overline{\mu}_1$ and $\overline{v}_1' = \overline{v}_1$. With the help of these formulae one proves the transformation properties of the charge and current densities (19) and the electric and magnetic polarizations (21):

$$\varrho^{e'}(R', t') = \varrho^e(R, t),$$
$$J'(R', t') = J(R, t) + V \varrho^e(R, t), \tag{25}$$

$$P'(R', t') = P(R, t),$$
$$M'(R', t') = M(R, t) - c^{-1} V \wedge P(R, t). \tag{26}$$

From (23) and (25) one proves the covariance of the charge conservation law (16). Furthermore from (23), (25) and (26) one finds that the field equations are covariant if one imposes the transformation formulae for the fields

$$E'(R', t') = E(R, t) - c^{-1} V \wedge B(R, t),$$
$$B'(R', t') = B(R, t) + c^{-1} V \wedge E(R, t). \tag{27}$$

We note again that in the present non-relativistic theory only terms up to order c^{-1} are included. As a consequence the transformation formula for the electric field contains in fact only the external magnetic field B_e, since the magnetic field generated by the sources is itself of order c^{-1}, as follows from the solution (17).

In a fashion analogous to the definition of the macroscopic charge density, which was the average of the atomic charge density, one can define macroscopic electric and magnetic multipole densities as:

$$\overline{\mathscr{P}}^{(n)} = \left\langle \sum_k \overline{\mu}_k^{(n)} \delta(R_k - R) \right\rangle = \sum_a \int \overline{\mu}_1^{(n)} f_1^a(R, 1; t) \mathrm{d}1 \equiv \sum_a \overline{\mathscr{P}}_a^{(n)},$$

$$\overline{\mathscr{M}}^{(n)} = \left\langle \sum_k \overline{\nu}_k^{(n)} \delta(R_k - R) \right\rangle = \sum_a \int \overline{\nu}_1^{(n)} f_1^a(R, 1; t) \mathrm{d}1 \equiv \sum_a \mathscr{M}_a^{(n)}, \quad (28)$$

where n indicates the multipole order: $n = 1$ dipole, $n = 2$ quadrupole, etc. These macroscopic multipole densities are functions of space and time coordinates R and t.

The expression (20) or (21) for the electric polarization vector P can be written in terms of the electric multipole densities (28)

$$P = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \overline{\mathscr{P}}^{(n)} = \overline{\mathscr{P}}^{(1)} - \nabla \cdot \overline{\mathscr{P}}^{(2)} + \nabla\nabla : \overline{\mathscr{P}}^{(3)} - \dots . \quad (29)$$

The right-hand side is a series expansion involving all multipole densities.

In the Maxwell equations (13) appear, besides ϱ^e and P, also the current density J and the magnetization vector M. The latter quantity, which is given in (20) or (21), cannot be expressed in terms of the multipole densities (28) alone, just as the current density cannot be expressed in terms of the charge density. In both cases the reason is that the atomic velocities v_k appear in a particular way as the expressions (18–19) and (20–21) for J and M show. It is convenient for the physical discussion to resolve the atomic velocity $v_k \equiv \beta_k c$ into a local mean velocity $v \equiv \beta c$ and a velocity fluctuation $\hat{v}_k \equiv \hat{\beta}_k c$:

$$v_k = v + \hat{v}_k. \quad (30)$$

(The local mean velocity is in general still a function of space and time coordinates R and t.) Then with the expression in (19) for the charge density one can write the current density of (19) as

$$J = \varrho^e v + \sum_a \int e_a \hat{v}_1 f_1^a(R, v_1; t) \mathrm{d}v_1 \equiv \varrho^e v + I. \quad (31)$$

In this way J has been resolved into a 'convection' current $\varrho^e v$ and a 'conduction' current I. The fact that the former produces a magnetic field as well has been demonstrated experimentally by Rowland[1].

Similarly (30) can be used in the expression (21) for the magnetization vector M. Then, using the definitions of the multipole densities (28), one can write

$$M = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \left\{ \mathscr{M}^{(n)} + \overline{\mathscr{P}}^{(n)} \wedge \beta + \sum_a \int \overline{\mu}_1^{(n)} \wedge \hat{\beta}_1 f_1^a(R, 1; t) \mathrm{d}1 \right\}, \quad (32)$$

because differentiation and averaging commute.

Alternatively, with the help of expression (29) for the polarization vector, the magnetization vector reads

$$M = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \mathscr{M}^{(n)} + P \wedge \beta$$
$$+ \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \sum_a \int \overline{\mu}_1^{(n)} \wedge \hat{\beta}_1 f_1^a(R, 1; t) \mathrm{d}1. \quad (33)$$

The physical significance of special cases of these forms will be discussed in the next section, where practical examples are treated. But it may be remarked already here that M shows three contributions, 1st: a sum which contains all magnetic multipole densities, analogous in structure to the series in the electric polarization (29), 2nd: a convection term due to the convection motion $v \equiv \beta c$ of the total polarization vector P, and 3rd: a fluctuation term, which contains the atomic electric multipole moments $\overline{\mu}_k^{(n)}$ and the velocity fluctuations $\hat{\beta}_k c$. The last term plays a role if the carriers of electric multipole moments $\overline{\mu}_k^{(n)}$ do not all have the same velocity (i.e. if $\hat{\beta}_k \neq 0$). Mazur and Nijboer[2] gave the first example of such a term. Expression (32) shows explicitly that M cannot be expressed in terms of the multipole densities (28) alone: the first and the second terms are functions of these multipole densities, but not the third.

Let us summarize the general results obtained so far. The Maxwell equations were found in the form of the set (13). It contains the macroscopic fields E and B, and moreover the four macroscopic quantities ϱ^e, J, P and M, for which expressions were found:

(a) The charge density ϱ^e, given as the average of the atomic charge density in formula (18) or (19).

[1] H. A. Rowland, Am. J. Sci. **15**(1878)30.

[2] P. Mazur and B. R. A. Nijboer, Physica **19**(1953)971; cf. reviews by P. Mazur, Adv. Chem. Phys. **1**(1958)309 and S. R. de Groot, The Maxwell equations (North-Holland Publ. Co., Amsterdam 1969).

(b) The current density J, given as the sum (31) of a convection current, due to the bulk motion of the charge density, and a conduction current, due to the fluctuations in the velocities of the atomic charges.

(c) The electric polarization vector P, expressed as a series expansion (29) in the macroscopic electric multipole densities defined in (28).

(d) The magnetic polarization vector M, given by (33). It contains in the first place a series in the macroscopic magnetic multipole densities of (28). Furthermore two terms describing the effects of moving electric multipoles occur: a convection term, due to the bulk motion of the electric polarization, and a fluctuation (or conduction) term, due to the fluctuations in the velocities of the atomic electric multipole moments.

4   Applications

a. *The polarizations up to dipole moments*

To simplify the discussion of the various physical systems let us give some explicit formulae, containing lowest order multipoles. In fact in not too dense systems one can limit oneself to the consideration of atomic charges and dipole moments only. Then the polarizations (21) become

$$P = \sum_a \int \overline{\mu}_1^{(1)} f_1^a(R, 1; t)\mathrm{d}1,$$

$$M = \sum_a \int (\overline{\nu}_1^{(1)} + \overline{\mu}_1^{(1)} \wedge \beta_1) f_1^a(R, 1; t)\mathrm{d}1. \tag{34}$$

In these expressions occur the macroscopic electric dipole density $\overline{\mathscr{P}}^{(1)}$ and the macroscopic magnetic dipole density $\overline{\mathscr{M}}^{(1)}$, defined in (28). With the use of these quantities, and the splitting of the atomic velocity in a local mean velocity βc and a deviation $\hat{\beta}_k c$ from it, one can write the polarizations as

$$P = \overline{\mathscr{P}}^{(1)},$$

$$M = \overline{\mathscr{M}}^{(1)} + \overline{\mathscr{P}}^{(1)} \wedge \beta + \sum_a \int \overline{\mu}_1^{(1)} \wedge \hat{\beta}_1 \, f_1^a(R, 1; t)\mathrm{d}1. \tag{35}$$

The electric polarization vector P could be expressed in terms of the macroscopic electric dipole density alone. The magnetic polarization vector M contains the magnetic dipole density. Furthermore terms due to moving electric dipoles are present. First a convection term, due to the bulk velocity $v = \beta c$

of the electric dipole density, is present. Its curl, which occurs in the Maxwell equations, is called the Röntgen current. It has been observed experimentally[1]. But M contains also terms due to the fluctuations $\hat{\beta}_k c$ in the velocity of the carriers of the electric dipole moments.

Only if the carriers of the electric dipole moments all have the same velocity $\beta_k = \beta$ do the fluctuation terms vanish. The polarizations then reduce to

$$P = \overline{\mathscr{P}}^{(1)}, \qquad M = \overline{\mathscr{M}}^{(1)} + \overline{\mathscr{P}}^{(1)} \wedge \beta. \tag{36}$$

These expressions are the same as Lorentz's original results[2]. Lorentz's model did not include the possibility of the appearance of the fluctuation terms. It should be noted that in contrast with the general formulae the special expressions (36) are functions of the macroscopic dipole densities alone.

If the system is completely at rest, i.e. if all atoms have velocities $\beta_k = 0$, then (36) further reduces to

$$P = \overline{\mathscr{P}}^{(1)}, \qquad M = \overline{\mathscr{M}}^{(1)}. \tag{37}$$

b. *The polarizations up to quadrupole moments*

In the dipole plus quadrupole approximation one retains the terms with $n = 1$ and 2 in (21):

$$P = \sum_a \int \overline{\mu}_1^{(1)} f_1^a(R, 1; t)\mathrm{d}1 - \sum_a \nabla \cdot \int \overline{\mu}_1^{(2)} f_1^a(R, 1; t)\mathrm{d}1,$$

$$M = \sum_a \int (\overline{\nu}_1^{(1)} + \overline{\mu}_1^{(1)} \wedge \beta_1) f_1^a(R, 1; t)\mathrm{d}1$$
$$- \sum_a \nabla \cdot \int (\overline{\nu}_1^{(2)} + \overline{\mu}_1^{(2)} \wedge \beta_1) f_1^a(R, 1; t)\mathrm{d}1. \tag{38}$$

Introducing the macroscopic dipole and quadrupole densities (28) with $n = 1$ and 2, and resolving the atomic velocity $\beta_k c$ into a local mean velocity βc and a velocity fluctuation $\hat{\beta}_k c$ one can write (38) as

$$P = \overline{\mathscr{P}}^{(1)} - \nabla \cdot \overline{\mathscr{P}}^{(2)},$$

$$M = \overline{\mathscr{M}}^{(1)} - \nabla \cdot \overline{\mathscr{M}}^{(2)} + (\overline{\mathscr{P}}^{(1)} - \nabla \cdot \overline{\mathscr{P}}^{(2)}) \wedge \beta + \sum_a \int \overline{\mu}_1^{(1)} \wedge \hat{\beta}_1 \, f_1^a(R, 1; t)\mathrm{d}1$$
$$- \sum_a \nabla \cdot \int \overline{\mu}_1^{(2)} \wedge \hat{\beta}_1 \, f_1^a(R, 1; t)\mathrm{d}1. \tag{39}$$

[1] W. C. Röntgen, Ann. Phys. Chem. **35**(1888)264, **40**(1890)93; A. Eichenwald, Ann. Phys. Chem. **11**(1903)1, 421.

[2] H. A. Lorentz, Proc. Roy. Acad. Amsterdam (1902)254; Enc. Math. Wiss. V 2, fasc. 1 (Teubner, Leipzig 1904) 200.

The electric polarization vector P is equal to the macroscopic electric dipole density minus the divergence of the electric quadrupole density. The magnetization contains three dipole contributions; the first is the macroscopic magnetic dipole density, the second is a convection term due to the bulk motion of the macroscopic electric dipole density $\overline{\mathscr{P}}^{(1)}$, and the third is a fluctuation term, due to the fluctuations in the velocities of the individual atomic dipole moments $\overline{\mu}_k^{(1)}$. This last term plays a role in systems in which the electric dipoles do not all have the same velocity. (In the following sections some practical examples will be given.) In all terms the negative divergence of a quadrupole term is added to the corresponding dipole terms. In uniform systems the quadrupole terms will thus not play a role, but for instance boundaries will give quadrupole (and perhaps even higher multipole order) contributions.

If all electric multipoles have the same velocity ($\beta_k = \beta$, the fluctuation terms disappear from the expressions for the magnetization vector M. Formulae (39) then simplify to

$$P = \overline{\mathscr{P}}^{(1)} - \nabla\cdot\overline{\mathscr{P}}^{(2)},$$
$$M = \overline{\mathscr{M}}^{(1)} - \nabla\cdot\overline{\mathscr{M}}^{(2)} + (\overline{\mathscr{P}}^{(1)} - \nabla\cdot\overline{\mathscr{P}}^{(2)})\wedge\beta. \qquad (40)$$

These expressions were originally found by Frenkel[1]. They include quadrupolar effects, but otherwise their validity is limited in the same way as Lorentz's, since the fluctuation terms of (39) are missing. Earlier Fokker[2] found these formulae, but without the magnetic quadrupole term.

For the still more special case of no motion at all ($\beta_k = 0$), the expressions further reduce to

$$P = \overline{\mathscr{P}}^{(1)} - \nabla\cdot\overline{\mathscr{P}}^{(2)}, \qquad M = \overline{\mathscr{M}}^{(1)} - \nabla\cdot\overline{\mathscr{M}}^{(2)}. \qquad (41)$$

Full symmetry between electric and magnetic terms is present only in this last static case. Rosenfeld[3] obtained these expressions but without the magnetic quadrupole term.

c. *Examples*

In this subsection the Maxwell equations for specific physical systems will be discussed. The expressions for the material quantities which occur in the

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[1] J. Frenkel, Lehrbuch der Elektrodynamik II (Springer, Berlin 1928), p. 26.
[2] A. D. Fokker, Phil. Mag. **39**(1920)404; Versl. Kon. Acad. Wet. Amsterdam **28**(1920) 1040; Relativiteitstheorie (Noordhoff, Groningen 1929).
[3] L. Rosenfeld, Theory of electrons (North-Holland Publ. Co., Amsterdam 1951); cf. J. Voisin, Physica **25**(1959)195.

Maxwell equations, namely the charge and current densities ϱ^e and J, and the electric and magnetic polarization vectors P and M, will depend on the characteristics of the particular physical model studied.

(i) *Metals.* A metal is supposed to consist of free electrons moving in a rigid lattice formed by positively charged ions. The 'stable groups' of point particles of the present theory are then those free electrons and ions. They will be labelled by an index $a = I$ and $a = II$ respectively. The model is then specified by assigning charges to the electrons, and charges and electric and magnetic dipole moments to the ions. Furthermore in the model one supposes that the metal can only move as a whole, with a velocity $v \equiv \beta c$. This means that all ions move with this velocity. The free electrons however have velocities $\beta_1 c = \beta c + \hat{\beta}_1 c$. On the basis of these properties of the model we can now give the expressions for the material quantities ϱ^e, J, P and M, which occur in the Maxwell equations. The charge density (19) becomes

$$\varrho^e = e_I f_1^I(R, t) + e_{II} f_1^{II}(R, t). \qquad (42)$$

The current density (31) is

$$J = \varrho^e v + I, \qquad I = e_I \int \hat{\beta}_1 c f_1^I(R, 1; t)d1. \qquad (43)$$

The convection current $\varrho^e v$ contains contributions (42) from the free electrons and the ions. The conduction current I contains only contributions from the free electrons, since the ions have no velocity fluctuations. The polarization vectors P and M follow from the formulae (36) for the dipole case, with the macroscopic dipole densities (28), as

$$P = \overline{\mathscr{P}}_{II}^{(1)}, \qquad M = \overline{\mathscr{M}}_{II}^{(1)} + \overline{\mathscr{P}}_{II}^{(1)}\wedge\beta. \qquad (44)$$

Only the ions contribute. Since the ions have no velocity fluctuations no fluctuation contribution arises in M. The free electrons do not give rise to such a contribution either, because, although they do have velocity fluctuations, they possess no dipole moments. This is the reason why the expressions (44) turn out to be of the particular type (36). The latter were also Lorentz's results. So for the model of the metal – and Lorentz apparently had this model in mind – these results are justified from the general theory.

A possible influence of multipole moments of higher than dipole order might have been taken into consideration. However in a system in which the total charges of 'stable groups' play a role, their effects usually overshadow those due to the dipole moments. The corrections obtained by taking into account also quadrupole effects are then negligibly small.

(ii) *Insulators.* If the stable groups in insulators are positively and negatively charged ions of the kind I and II, then the model can be specified as follows. The ions possess charges as well as electric and magnetic multipole moments of order $n = 1, 2, \ldots$. The system is a rigid lattice moving with the velocity $v = \beta c$ as a whole. This means that the ions have this velocity, so that all velocity fluctuations vanish. Often the charges of the two kinds of ions just cancel so that the system as a whole is electrically neutral. Then we have the charge density $\varrho^e = 0$, just as for an atomic or molecular lattice. The current density J (31) also vanishes because both the convection current $\varrho^e v$ and the conduction current I are zero: the first because $\varrho^e = 0$, and the second because all velocity fluctuations vanish. Since the ion lattice is usually fairly closely packed, one may need to include terms of higher than dipole order into the polarizations. Because no fluctuation motion is present, the expressions (29) and (32) become

$$P = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} \vdots \, \overline{\mathscr{P}}^{(n)},$$

$$M = \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} \vdots \, (\overline{\mathscr{M}}^{(n)} + \overline{\mathscr{P}}^{(n)} \wedge \beta), \qquad (45)$$

with the complete multipole series. One has here for the macroscopic multipole densities:

$$\overline{\mathscr{P}}^{(n)} = \overline{\mathscr{P}}_{\mathrm{I}}^{(n)} + \overline{\mathscr{P}}_{\mathrm{II}}^{(n)}, \qquad \overline{\mathscr{M}}^{(n)} = \overline{\mathscr{M}}_{\mathrm{I}}^{(n)} + \overline{\mathscr{M}}_{\mathrm{II}}^{(n)}. \qquad (46)$$

The number of space differentiations in (45) increases with the multipole order. The effects of the higher order multipole densities show up especially at boundaries between different media.

(iii) *Plasmas.* A plasma is a gas in which a sensible proportion of the atoms or molecules is ionized, so that virtually the properties of the system are completely determined by the effects of the charges of the ions and free electrons. In fact in practice one neglects completely the multipole moments of the atoms, molecules and ions. In such a model the charges of the ions and free electrons determine the value of the charge–current densities ϱ^e and J, which are given by (18). If all multipole moments are neglected, the polarization vectors P and M vanish. The Maxwell equations (13) read then

$$\begin{aligned}
\nabla \cdot E &= \varrho^e, \\
-\partial_0 E + \nabla \wedge B &= c^{-1} J, \\
\nabla \cdot B &= 0, \\
\partial_0 B + \nabla \wedge E &= 0.
\end{aligned} \qquad (47)$$

These equations form indeed the starting point which is generally adopted in plasma theory. In this connexion it should be noted that sometimes electric polarization vectors are introduced that are not defined as the average over the microscopic electric multipole moments. As a matter of fact various 'effective polarization vectors' can be found in literature. One of these is the 'effective polarization vector' P^*, which is related to the charge density ϱ^e as

$$\varrho^e = -\nabla \cdot P^*. \qquad (48)$$

Then one introduces also an 'effective displacement vector' D^*, defined as

$$D^* = E + P^*. \qquad (49)$$

Another formal 'effective displacement vector' which is sometimes used is the quantity D^{**}, which satisfies

$$\partial_0 D^{**} = \partial_0 E + c^{-1} J. \qquad (50)$$

Then one can accordingly also introduce 'effective dielectric constants'. The dielectric constants E are normally defined as the proportionality constants between the fields D and E. The 'effective constants' ε^* or ε^{**} are defined as the proportionality constants between the fields D^* or D^{**} and E. Some of these 'effective' quantities may be useful abbreviations in certain cases, but one should not confuse them with the ordinary polarization and displacement vectors, which are directly connected to the multipole moments of the particles in the system.

In particular the model of a plasma is such that the refractive index n is different from unity, whereas $\varepsilon = 1$, since $D = E$. In fact for a plasma n^2 is therefore not equal to ε. Again one can of course introduce an 'effective dielectric constant' equal to the square of the refractive index, but one should not confuse it with the ordinary dielectric constant ε.

(iv) *Fluids.* In a fluid which consists of neutral molecules the charge density ϱ^e and current density J both vanish. The polarizations P and M contain contributions from the various molecular multipole moments.

In a gas it is usual to limit oneself to the dipole contributions alone. The velocity $\beta_k c$ of the molecules will again be written as the sum of a local mean velocity βc (which depends on space and time coordinates R and t) and a velocity fluctuation $\hat{\beta}_k c$. Then the dipole approximation (35) for the polarization vectors applies. The electric polarization vector is simply equal to the electric dipole density $\overline{\mathscr{P}}^{(1)}$. The magnetic polarization vector contains

three contributions. The first is the magnetic dipole density; the second is a 'convection term' and the third has a fluctuation character: even for a gas at rest this term will not disappear.

In a liquid, because of its high density, one may need to take into account the effects of higher multipole moments, for instance the quadrupole moments. In the latter case the polarizations are given by (39).

(v) *Electrolytes.* In an electrolyte one has positively and negatively charged ions, and usually also a neutral component. In this respect it is similar to a plasma. However the density of an electrolyte is much higher than the density of a plasma. The effects of dipoles (or even higher order multipoles) should therefore be taken into account. The model adopted here is a mixture of three components labelled by the indices I, II and III of which I and II are ions, with charges e_I and e_{II}, and III neutral molecules; all three components are supposed to carry electric and magnetic dipole moments.

The charge density (19) gets the form

$$\varrho^e = \sum_{a=I}^{II} e_a f_1^a(\boldsymbol{R}; t). \tag{51}$$

The velocities of the ions and molecules can be written as the sum of a local mean velocity of all ions and molecules and fluctuation velocities. Then the current density (31) is

$$\boldsymbol{J} = \varrho^e \boldsymbol{v} + \boldsymbol{I}, \tag{52}$$

where $\varrho^e \boldsymbol{v}$ is the convection current and $\boldsymbol{I}$ the conduction current:

$$\boldsymbol{I} = \sum_{a=1}^{II} \int e_a \hat{\boldsymbol{v}}_1 f_1^a(\boldsymbol{R}, \boldsymbol{v}_1; t) \mathrm{d}\boldsymbol{v}_1. \tag{53}$$

With the macroscopic electric and magnetic dipole densities (21) for the ions and the molecules $\overline{\mathscr{P}}_a^{(1)}$ and $\overline{\mathscr{M}}_a^{(1)}$ (a = I, II, III) one can write the polarization vectors (35) as

$$\boldsymbol{P} = \sum_{a=I}^{III} \overline{\mathscr{P}}_a^{(1)},$$

$$\boldsymbol{M} = \sum_{a=I}^{III} \left\{ \overline{\mathscr{M}}_a^{(1)} + \overline{\mathscr{P}}_a^{(1)} \wedge \boldsymbol{\beta} + \int \overline{\mu}_1^{(1)} \wedge \hat{\boldsymbol{\beta}}_1 f_1^a(\boldsymbol{R}, 1; t) \mathrm{d}1 \right\}. \tag{54}$$

The polarization vector $\boldsymbol{P}$ contains the three electric dipole densities. The magnetization vector $\boldsymbol{M}$ consists of three kinds of terms. First the magnetic dipole densities due to the ions and molecules appear. Then the convection

of the electric dipole densities with the bulk velocity $\boldsymbol{v} = \boldsymbol{\beta} c$ gives a contribution. Finally the electric dipoles also have fluctuations in their velocities around the bulk motion. These effects give rise to the last term. They do not occur in solids, but they can play a role in fluid systems, in which freely moving electric multipoles exist.

5   The momentum and energy equations

a. *Introduction*

The motion of matter in bulk is described by the balance equations of momentum, energy and angular momentum. The derivation of the former two from the corresponding atomic laws by means of a statistical averaging procedure will be the subject of this section, while the latter will be discussed separately in the following section. As a result we shall find macroscopic laws that contain quantities, such as the pressure, the internal energy and the heat flow, which are given as statistical averages of atomic quantities.

In contrast to the field equations the material equations mentioned contain quantities that are two-point functions on the atomic level, so that they contain two-point distribution functions (or correlation functions) on the macroscopic level. As a consequence one will have to distinguish in the course of the treatment between physical systems for which these correlation functions show marked differences: systems in which the correlations have short range – such as gases, liquids, plasmas and amorphous or polycrystalline solids – and systems such as crystalline solids with correlation functions of long range character.

b. *The mass conservation law*

In the course of the derivation of the momentum and energy laws, we shall need the macroscopic mass conservation law, which is an immediate consequence of the atomic conservation law. In fact, the atomic mass density is

$$\rho(\boldsymbol{R}, t) = \sum_k m_k \delta(\boldsymbol{R}_k - \boldsymbol{R}), \tag{55}$$

where m_k is the mass of the (identical) atoms for a one-component system[1].

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[1] For formal convenience we treat in the following subsections one-component systems. The generalization to mixtures is obvious (cf. subsection *g*).

Then the macroscopic mass density becomes:

$$\varrho(R, t) = \langle \sum_k m_k \delta(R_k - R) \rangle \equiv m f_1(R; t),\qquad (56)$$

where $f_1(R; t)$ is a one-point distribution function, which depends only on the position $R_1 \,(= R)$ and the time. The time derivative of the macroscopic mass density (56) is according to (2)

$$\frac{\partial \varrho}{\partial t} = \langle \sum_k m_k v_k \cdot \nabla_k \delta(R_k - R) \rangle,\qquad (57)$$

since in this case $d/dt = v_k \cdot \nabla_k$ (with v_k the atomic velocity $\dot{R}_k$). Introducing the local barycentric velocity $v(R, t)$ by

$$\varrho(R, t)v(R, t) = \langle \sum_k m_k v_k \delta(R_k - R) \rangle \equiv \int m v_1 f_1(R, v_1; t)dv_1,\qquad (58)$$

we may write (57) in the form

$$\frac{\partial \varrho}{\partial t} = -\nabla \cdot (\varrho v),\qquad (59)$$

which is the macroscopic law of mass conservation.

c. *The momentum balance*

The momentum law is obtained by taking the time derivative of (58). With (2) and the equation of motion (I.50) one gets

$$\frac{\partial \varrho v}{\partial t} = -\nabla \cdot \langle \sum_k m_k v_k v_k \delta(R_k - R) \rangle + \langle \sum_k (f_k^L + f_k^S)\delta(R_k - R) \rangle.\qquad (60)$$

Introducing the velocity fluctuation $\hat{v}_k$ as

$$\hat{v}_k(R, t) \equiv v_k - v(R, t),\qquad (61)$$

we obtain from (60) with (56) and (58) the momentum balance equation

$$\frac{\partial \varrho v}{\partial t} = -\nabla \cdot (\varrho v v + \mathbf{P}^K) + F^L + F^S,\qquad (62)$$

where the kinetic pressure

$$\mathbf{P}^K \equiv \int m \hat{v}_1 \hat{v}_1 f_1(R, v_1; t)dv_1\qquad (63)$$

is written with the help of an appropriate one-point distribution function. Furthermore we introduced the abbreviations $F^L \equiv \langle \sum_k f_k^L \delta(R_k - R) \rangle$ and $F^S \equiv \langle \sum_k f_k^S \delta(R_k - R) \rangle$ for the long and short range terms.

The *long range* term contains f_k^L, which has been specified in (I.54). We shall first treat the part with the external fields (E_e, B_e) (it will be called F_e^L). It can be expressed in terms of the macroscopic charge and current densities (v. (18)):

$$\varrho^e(R, t) = \langle \sum_k e_k \delta(R_k - R) \rangle,\qquad J(R, t) = \langle \sum_k e_k v_k \delta(R_k - R) \rangle,\qquad (64)$$

(where $e_k = e$ is the charge of the (identical) atoms) and the macroscopic polarization and magnetization densities which read, if only dipoles contribute for the system under consideration (v. (20))[1]

$$P(R, t) = \langle \sum_k \bar{\mu}_k^{(1)}\delta(R_k - R) \rangle,$$

$$M(R, t) = \langle \sum_k (\bar{v}_k^{(1)} + \bar{\mu}_k^{(1)} \wedge v_k/c)\delta(R_k - R) \rangle.\qquad (65)$$

(Note that according to (I.30) the magnetization is of the order c^{-1}, while the other three densities are of the order c^0.) In this way we get the expression

$$F_e^L = \varrho^e E_e + c^{-1}J \wedge B_e + (\nabla E_e)\cdot P + (\nabla B_e)\cdot M$$

$$+ c^{-1}\langle \sum_k \frac{d}{dt}\{\bar{\mu}_k^{(1)} \wedge B_e(R_k, t)\}\delta(R_k - R) \rangle.\qquad (66)$$

The last term becomes with (2)

$$c^{-1}\frac{\partial}{\partial t}\langle \sum_k \bar{\mu}_k^{(1)} \wedge B_e \delta(R_k - R) \rangle + c^{-1}\nabla \cdot \langle \sum_k v_k \bar{\mu}_k^{(1)} \wedge B_e \delta(R_k - R) \rangle.\qquad (67)$$

If (61) and (65) are used in this expression and the result is substituted into (66), one gets

$$F_e^L = \varrho^e E_e + c^{-1}J \wedge B_e + (\nabla E_e)\cdot P + (\nabla B_e)\cdot M$$

$$+ c^{-1}\frac{\partial}{\partial t}(P \wedge B_e) + c^{-1}\nabla \cdot (vP \wedge B_e)$$

$$+ c^{-1}\nabla \cdot \int \hat{v}_1 \bar{\mu}_1^{(1)} \wedge B_e f_1(R, v_1, \bar{\mu}_1^{(1)}; t)dv_1 d\bar{\mu}_1^{(1)}.\qquad (68)$$

[1] Higher multipoles could be included at this point, v. problem 3 for the case of quadrupoles. As a result it turns out that the macroscopic force density which for the dipole case will be given in (106) can no longer be expressed in terms of the Maxwell fields and the total polarizations alone. (Cf. also H. A. Haus, Ann. Physics 45(1967)314.)

The remaining part of the long range term of (62), which is due to the interatomic interactions (v. (I.54)) may be written with the help of a two-point distribution function:

$$F^{\mathrm{L}}-F^{\mathrm{L}}_{\mathrm{e}} = -\int \sum_{n,m=0}^{\infty} \left(\overline{\boldsymbol{\mu}}_1^{(n)} : \nabla_1^n \overline{\boldsymbol{\mu}}_2^{(m)} : \nabla_2^m \nabla_1 \frac{1}{4\pi|R_1-R_2|}\right)$$
$$\delta(R-R_1)f_2(R_1,1,R_2,2;t)\mathrm{d}R_1\,\mathrm{d}1\,\mathrm{d}R_2\,\mathrm{d}2, \quad (69)$$

where 1 (and 2) denote the whole set of electric multipole moments $\overline{\boldsymbol{\mu}}_1^{(n)}$ (and $\overline{\boldsymbol{\mu}}_2^{(m)}$) with $n, m = 0, 1, \ldots$. Let us split the right-hand side into two parts with the help of (7). In the 'uncorrelated' part, which contains the product of one-point distribution functions, we add a factor $\delta(R'-R_2)$ and an integration over R'. Furthermore we introduce the macroscopic charge and polarization densities (64–65), omitting here all multipole moments of order two and higher. The latter moments would give rise to terms containing the macroscopic multipole densities of order two and higher, which are assumed to be negligible in our system. In the 'correlated' part (which contains the correlation function) the integration over R_1 may be performed. In this way we obtain:

$$F^{\mathrm{L}}-F^{\mathrm{L}}_{\mathrm{e}} = -\int \{\varrho^{\mathrm{e}}(R,t)+P(R,t)\cdot\nabla\}\{\varrho^{\mathrm{e}}(R',t)+P(R',t)\cdot\nabla'\}\nabla\frac{1}{4\pi|R-R'|}\,\mathrm{d}R'$$
$$-\int \sum_{n,m=0}^{\infty} \left(\overline{\boldsymbol{\mu}}_1^{(n)} : \nabla^n \overline{\boldsymbol{\mu}}_2^{(m)} : \nabla'^m \nabla \frac{1}{4\pi|R-R'|}\right) c_2(R,1,R',2;t)\mathrm{d}R'\,\mathrm{d}1\,\mathrm{d}2.$$
$$(70)$$

The total long range force density is now given by the sum of (68) and (70). Introducing the macroscopic electric and magnetic fields (17), which read up to order c^{-1} and c^0 respectively:

$$E(R,t) = E_{\mathrm{e}}(R,t)-\int\{\varrho^{\mathrm{e}}(R',t)+P(R',t)\cdot\nabla'\}\nabla\frac{1}{4\pi|R-R'|}\,\mathrm{d}R', \quad (71)$$

$$B(R,t) = B_{\mathrm{e}}(R,t),$$

(v. problem 1) we obtain thus up to order c^{-1}

$$F^{\mathrm{L}} = \varrho^{\mathrm{e}}E+c^{-1}J\wedge B+(\nabla E)\cdot P+(\nabla B)\cdot M$$
$$+c^{-1}\frac{\partial}{\partial t}(P\wedge B)+c^{-1}\nabla\cdot(vP\wedge B)-\nabla\cdot P^{\mathrm{F}}+F^{\mathrm{C}}, \quad (72)$$

with

$$P^{\mathrm{F}} \equiv -c^{-1}\int \hat{v}_1\,\overline{\boldsymbol{\mu}}_1^{(1)}\wedge Bf_1(R,v_1,\overline{\boldsymbol{\mu}}_1^{(1)};t)\mathrm{d}v_1\,\mathrm{d}\overline{\boldsymbol{\mu}}_1^{(1)}, \quad (73)$$

a contribution to the pressure tensor due to the action of the field B on the electric dipoles. Furthermore F^{C} is the 'correlation contribution' given by the last term in (70). It reads written with s for the interatomic separation $R-R'$:

$$F^{\mathrm{C}} \equiv -\int \sum_{n,m=0}^{\infty} \left\{(-1)^m\overline{\boldsymbol{\mu}}_1^{(n)} : \nabla_s^n\overline{\boldsymbol{\mu}}_2^{(m)} : \nabla_s^m\nabla_s\frac{1}{4\pi s}\right\}$$
$$c_2(R,1,R-s,2;t)\,\mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2. \quad (74)$$

The *short range* term $F^{\mathrm{S}} \equiv \langle \sum_k f_k^{\mathrm{S}}\delta(R_k-R)\rangle$ at the right-hand side of (62) contains the force f_k^{S} given in (I.52). We may write it with the help of an appropriate two-point distribution function. Again performing the integration over R_1 and introducing the integration variable $s = R-R_2$ we get with $r_{ki} \equiv R_{ki}-R_k$:

$$F^{\mathrm{S}} = \int \left\{-\sum_{i,j}\nabla_s\frac{e_ie_j}{4\pi|s+r_{1i}-r_{2j}|} + \sum_{n,m=0}^{\infty}(-1)^m\overline{\boldsymbol{\mu}}_1^{(n)} : \nabla_s^n\overline{\boldsymbol{\mu}}_2^{(m)} : \nabla_s^m\nabla_s\frac{1}{4\pi s}\right\}$$
$$f_2(R,1,R-s,2;t)\mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2, \quad (75)$$

where e_i and e_j are the charges of the constituent particles i and j of the (identical) atoms.

The equation (62) with (63) and (72–75) constitutes the macroscopic balance of momentum. It will be studied further for specific systems in subsections f, g and h.

d. *The energy balance*

The macroscopic energy law will be derived from the atomic energy equation (I.63). Let us first consider the macroscopic quantity

$$\left\langle \sum_k \left(\tfrac{1}{2}m_kv_k^2+\tfrac{1}{2}\sum_i m_{ki}\dot{r}_{ki}^2+\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|r_{ki}-r_{kj}|}\right)\delta(R_k-R)\right\rangle \quad (76)$$

(v_k is the atomic velocity $\dot{R}_k$). Introducing the appropriate distribution functions, the notations m for the mass m_k of the (identical) atoms, and m_i and e_i for the mass m_{ki} and charge e_{ki} of their constituent particles i, one gets for this expression, with the help of (56), (58) and (61):

$$\tfrac{1}{2}\varrho v^2+\varrho u^{\mathrm{K}} \quad (77)$$

with an internal energy density

$$\varrho u^{\mathrm{K}} \equiv \int \left(\tfrac{1}{2}m\hat{v}_1^2+\tfrac{1}{2}\sum_i m_i\dot{r}_{1i}^2+\sum_{i,j(i\neq j)}\frac{e_ie_j}{8\pi|r_{1i}-r_{1j}|}\right)f_1(R,1;t)\mathrm{d}1, \quad (78)$$

due to the velocity fluctuations and the intra-atomic kinetic and potential energies.

The energy balance equation is obtained by taking the time derivative of (77) in its form (76) and by using (2) and (I.63):

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho v^2 + \varrho u^{K})$$

$$= -\nabla\cdot\left\langle \sum_{k} v_k \left(\tfrac{1}{2}m_k v_k^2 + \tfrac{1}{2}\sum_{i} m_{ki}\dot{r}_{ki}^2 + \sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}}{8\pi|r_{ki}-r_{kj}|}\right)\delta(R_k - R)\right\rangle$$

$$+\left\langle \sum_{k}(\psi_k^{L}+\psi_k^{S})\delta(R_k-R)\right\rangle. \quad (79)$$

Splitting the atomic velocities according to (61) one obtains with the help of appropriate distribution functions the energy balance equation:

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho v^2 + \varrho u^{K}) = -\nabla\cdot\{v(\tfrac{1}{2}\varrho v^2 + \varrho u^{K}) + \mathbf{P}^{K}\cdot v + J_q^{K}\} + \Psi^{L}+\Psi^{S}, \quad (80)$$

with $\mathbf{P}^{K}$ the kinetic pressure given in (63) and

$$J_q^{K} \equiv \int \hat{v}_1 \left(\tfrac{1}{2}m\hat{v}_1^2 + \tfrac{1}{2}\sum_{i} m_i \dot{r}_{1i}^2 + \sum_{i,j(i\neq j)}\frac{e_i e_j}{8\pi|r_{1i}-r_{1j}|}\right)f_1(R, 1; t)\mathrm{d}1, \quad (81)$$

a contribution to the heat flow. (In fact it is due to the transport, with the velocity fluctuation, of the atomic quantity occurring in (78).) Furthermore the last two terms of (80) represent long and short range contributions defined as $\Psi^{L,S} = \langle\sum_{k}\psi_k^{L,S}\delta(R_k-R)\rangle$, with $\psi_k^{L,S}$ as specified in (I.66) and (I.65). They will now be investigated in detail.

The *long range* part contains a contribution due to the external fields (E_e, B_e) which may be written in the form

$$\Psi_e^{L} = J\cdot E_e - M\cdot\frac{\partial B_e}{\partial t} + \left\langle \sum_{k}\{v_k\cdot(\nabla_k E_e)\cdot\bar{\mu}_k^{(1)} + \dot{\bar{\mu}}_k^{(1)}\cdot E_e\}\delta(R_k-R)\right\rangle, \quad (82)$$

where (64) and (65) have been used. With the help of (2) one may write

$$\left\langle \sum_{k}\dot{\bar{\mu}}_k^{(1)}\delta(R_k-R)\right\rangle = \frac{\partial}{\partial t}\left\langle \sum_{k}\bar{\mu}_k^{(1)}\delta(R_k-R)\right\rangle + \nabla\cdot\left\langle \sum_{k} v_k \bar{\mu}_k^{(1)}\delta(R_k-R)\right\rangle. \quad (83)$$

Using this identity and (65) we get for (82):

$$\Psi_e^{L} = J\cdot E_e + \frac{\partial P}{\partial t}\cdot E_e - M\cdot\frac{\partial B_e}{\partial t} + \nabla\cdot\{\langle\sum_{k} v_k \bar{\mu}_k^{(1)}\delta(R_k-R)\rangle\cdot E_e\}. \quad (84)$$

Introducing velocity fluctuations (61) and the appropriate distribution functions, and using again (65), we obtain finally

$$\Psi_e^{L} = J\cdot E_e + \frac{\partial P}{\partial t}\cdot E_e + \nabla\cdot(vP\cdot E_e) - M\cdot\frac{\partial B_e}{\partial t}$$

$$+\nabla\cdot\left[\left\{\int \hat{v}_1\, \bar{\mu}_1^{(1)}f_1(R, v_1, \bar{\mu}_1^{(1)}; t, \mathrm{d}v_1\, \mathrm{d}\bar{\mu}_1^{(1)}\right\}\cdot E_e\right]. \quad (85)$$

The interatomic contribution to Ψ^{L} (v. the first term of (I.66)) reads, written with distribution functions,

$$\Psi^{L} - \Psi_e^{L} = -\int\left\{\sum_{m=0}^{\infty}(\sum_{n=0}^{\infty}\bar{\mu}_1^{(n)}:\nabla_1^n v_1\cdot\nabla_1 + \sum_{n=1}^{\infty}\bar{\mu}_1^{(n)}:\nabla_1^n)\bar{\mu}_2^{(m)}:\nabla_2^m\frac{1}{4\pi|R_1-R_2|}\right\}$$

$$\delta(R-R_1)f_2(R_1, 1, R_2, 2; t)\mathrm{d}R_1\, \mathrm{d}1\, \mathrm{d}R_2\, \mathrm{d}2. \quad (86)$$

With the help of (7) the right-hand side may be split into two parts. In the uncorrelated part we introduce the macroscopic charge and polarization densities (64–65) taking only dipole moments into account and using (61) and (83). Then we get:

$$\Psi^{L} - \Psi_e^{L} = -\int\left\{J(R, t) + \frac{\partial P(R, t)}{\partial t}\right\}\cdot\nabla\{\varrho^e(R', t) + P(R', t)\cdot\nabla'\}\frac{1}{4\pi|R-R'|}\mathrm{d}R'$$

$$-\nabla\cdot\int v(R, t)P(R, t)\cdot\nabla\{\varrho^e(R', t) + P(R', t)\cdot\nabla'\}\frac{1}{4\pi|R-R'|}\mathrm{d}R'$$

$$-\nabla\cdot\int \hat{v}_1\left[\bar{\mu}_1^{(1)}\cdot\nabla\{\varrho^e(R', t) + P(R', t)\cdot\nabla'\}\frac{1}{4\pi|R-R'|}\right]$$

$$f_1(R, v_1, \bar{\mu}_1^{(1)}; t)\mathrm{d}R'\, \mathrm{d}v_1\, \mathrm{d}\bar{\mu}_1^{(1)}$$

$$-\int\sum_{m=0}^{\infty}\left\{(\sum_{n=0}^{\infty}\bar{\mu}_1^{(n)}:\nabla_1^n v_1\cdot\nabla_1 + \sum_{n=1}^{\infty}\dot{\bar{\mu}}_1^{(n)}:\nabla_1^n)\bar{\mu}_2^{(m)}:\nabla_2^m\frac{1}{4\pi|R_1-R_2|}\right\}$$

$$\delta(R-R_1)c_2(R_1, 1, R_2, 2; t)\mathrm{d}R_1\, \mathrm{d}1\, \mathrm{d}R_2\, \mathrm{d}2. \quad (87)$$

The total long range contribution is the sum of (85) and (87). It reads written with the Maxwell fields (71) and the pressure $\mathbf{P}^{F}$ (73)

$$\Psi^{L} = J\cdot E + \frac{\partial P}{\partial t}\cdot E + \nabla\cdot(vP\cdot E) - M\cdot\frac{\partial B}{\partial t} - \nabla\cdot(\mathbf{P}^{F}\cdot v + J_q^{F}) + \Psi^{C}, \quad (88)$$

with

$$J_q^{F} \equiv -\left\{\int \hat{v}_1\, \bar{\mu}_1^{(1)}f_1(R, v_1, \bar{\mu}_1^{(1)}; t)\mathrm{d}v_1\, \mathrm{d}\bar{\mu}_1^{(1)}\right\}\cdot(E + c^{-1}v\wedge B), \quad (89)$$

a contribution to the heat flow due to the interaction of the fields (E, B) and the electric dipoles. Furthermore the correlation contribution Ψ^C given by the last term of (87) may be written as

$$\Psi^C \equiv -\int \sum_{m=0}^{\infty} (-1)^m \left\{ (\sum_{n=0}^{\infty} \overline{\mu}_1^{(n)} : \nabla_s^n v_1 \cdot \nabla_s + \sum_{n=1}^{\infty} \dot{\overline{\mu}}_1^{(n)} : \nabla_s^n) \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{4\pi s} \right\}$$
$$c_2(R, 1, R-s, 2; t) \mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2, \quad (90)$$

where the integration over R_1 has been performed and the variable $s \equiv R - R_2$ introduced.

The *short range* term $\Psi^S \equiv \langle \sum_k \psi_k^S \delta(R_k - R) \rangle$, where ψ_k^S is given in (I.65), may be written in terms of a two-point distribution function:

$$\Psi^S = -\int \left\{ \sum_{i,j} (v_1 + \dot{r}_{1i}) \cdot \nabla_s \frac{e_i e_j}{4\pi |s + r_{1i} - r_{2j}|} \right.$$
$$\left. - \sum_{m=0}^{\infty} (-1)^m (\sum_{n=0}^{\infty} \overline{\mu}_1^{(n)} : \nabla_s^n v_1 \cdot \nabla_s + \sum_{n=1}^{\infty} \dot{\overline{\mu}}_1^{(n)} : \nabla_s^n) \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{4\pi s} \right\}$$
$$f_2(R, 1, R-s, 2; t) \mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2. \quad (91)$$

The equation (80) with (78), (81), (88–91) is the balance equation of energy. The correlation and short range contributions (90) and (91) will be studied for special systems in the following subsections.

e. *The short range terms in the momentum and energy laws*

We shall consider in this subsection the terms F^S and Ψ^S occurring in the momentum and energy equations (62) and (80), and given explicitly in (75) and (91). Their short range character will allow us to write them in a convenient form.

Since the bracket expression in (75) vanishes if the atoms are outside each other the integral needs to be extended over small values of s only. In sufficiently homogeneous systems the two-point distribution function $f_2(R, 1, R-s, 2; t)$ in (75) varies slowly as a function of R, i.e. appreciably only over macroscopic distances whereas it varies rapidly as a function of the interatomic distance s. Hence one may limit oneself in the integral to the first two terms in a Taylor expansion of f_2 as a function of R [1]:

$$f_2(R, 1, R-s, 2; t)$$
$$= f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) - \tfrac{1}{2}s \cdot \nabla f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t), \quad (92)$$

[1] Cf. J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**(1950)817.

(with $\nabla \equiv \partial/\partial R$). In this way (75) becomes

$$F^S = -\nabla \cdot P^S \quad (93)$$

with the abbreviation

$$P^S \equiv -\int \left\{ s\nabla_s \left(\sum_{i,j} \frac{e_i e_j}{8\pi |s + r_{1i} - r_{2j}|} - \sum_{n,m=0}^{\infty} (-1)^m \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right) \right\}$$
$$f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) \mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2. \quad (94)$$

The latter quantity will turn out to be a contribution to the pressure tensor. Owing to the (trivial) symmetry of f_2 with respect to an interchange of the first pair of variables with the second pair, the first term of the right-hand side of (92) does not give rise to a term in (93).

Let us now turn to the discussion of the short range term Ψ^S (91) of the energy equation. The expression between brackets in (91) vanishes if the atoms are outside each other. With the use of the expansion (92) we obtain now

$$\Psi^S = \Psi^{S*} - \nabla \cdot (P^S \cdot v + J_q^{S'}). \quad (95)$$

The first term Ψ^{S*} reads like (91) but with $f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t)$ instead of $f_2(R, 1, R-s, 2; t)$, while the second contains, apart from a term with the local velocity v, a divergence of the vector

$$J_q^{S'} \equiv -\int s \left\{ \sum_{i,j} (\hat{v}_1 + \dot{r}_{1i}) \cdot \nabla_s \frac{e_i e_j}{8\pi |s + r_{1i} - r_{2j}|} \right.$$
$$\left. - \sum_{m=0}^{\infty} (-1)^m (\sum_{n=0}^{\infty} \overline{\mu}_1^{(n)} : \nabla_s^n \hat{v}_1 \cdot \nabla_s + \sum_{n=1}^{\infty} \dot{\overline{\mu}}_1^{(n)} : \nabla_s^n) \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right\}$$
$$f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) \mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2. \quad (96)$$

The contribution Ψ^{S*} to (95) may be written in a simpler form. For that purpose we shall consider the time derivative of the quantity

$$\varrho u^S \equiv \int \left(\sum_{i,j} \frac{e_i e_j}{8\pi |s + r_{1i} - r_{2j}|} - \sum_{n,m=0}^{\infty} (-1)^m \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right)$$
$$f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) \mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2, \quad (97)$$

which will turn out to be a contribution to the internal energy density. With the identity

$$\frac{\partial f_2(R+\frac{1}{2}s, r_{1i}, R-\frac{1}{2}s, r_{2j}; t)}{\partial t} = -\int \left\{ \frac{v_1+v_2}{2} \cdot \nabla + (v_1-v_2) \cdot \nabla_s \right.$$

$$\left. + \dot{r}_{1i} \cdot \nabla_{r_{1i}} + \dot{r}_{2j} \cdot \nabla_{r_{2j}} \right\} f_2(R+\frac{1}{2}s, v_1, r_{1i}, \dot{r}_{1i}, R-\frac{1}{2}s, v_2, r_{2j}, \dot{r}_{2j}; t)$$

$$\mathrm{d}v_1 \, \mathrm{d}v_2 \prod_{i,j} \mathrm{d}\dot{r}_{1i} \, \mathrm{d}\dot{r}_{2j}, \quad (98)$$

which follows from the conservation of the number of particles (or the probability in fluxion space), we get for the time derivative of (97) after partial integration and the use of the (trivial) symmetry $f_2(R+\frac{1}{2}s, 1, R-\frac{1}{2}s, 2; t) = f_2(R-\frac{1}{2}s, 2, R+\frac{1}{2}s, 1; t)$:

$$\frac{\partial \varrho u^S}{\partial t} = -\nabla \cdot (v\varrho u^S + J_q^{S''}) - \Psi^{S*} \quad (99)$$

with the abbreviation

$$J_q^{S''} \equiv \int (\hat{v}_1 + \hat{v}_2) \left(\sum_{i,j} \frac{e_i e_j}{16\pi|s+r_{1i}-r_{2j}|} - \sum_{n,m=0}^{\infty} (-1)^m \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{16\pi s} \right)$$

$$f_2(R+\frac{1}{2}s, 1, R-\frac{1}{2}s, 2; t) \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2. \quad (100)$$

The divergence in (99) contains a convective part $v\varrho u^S$ and the conductive part (100).

With Ψ^{S*} from (99) we get for (95):

$$\Psi^S = -\nabla \cdot (v\varrho u^S + \mathbf{P}^S \cdot v + J_q^S) - \frac{\partial \varrho u^S}{\partial t}. \quad (101)$$

Since Ψ^S occurred in the energy equation (80), it appears that ϱu^S (97) is a contribution to the internal energy density, and that J_q^S, which is the sum of $J_q^{S'}$ (96) and $J_q^{S''}$ (100), is a contribution to the heat flow.

In this way, the short range quantities F^S and Ψ^S, which occur in the momentum and energy equations, have been found, in formulae (93) and (101), for sufficiently homogeneous systems. It may be noted that if the 'atoms' carry charges, but no multipole moments (as in plasmas, for instance), the quantities F^S and Ψ^S simply vanish.

f. The momentum and energy equations for fluids

In this subsection we want to consider the momentum and energy equations for systems in which the correlation function has short range i.e.

$c_2(R, 1, R-s, 2; t)$ vanishes rapidly as the interatomic distance s increases. This is usually the case for one-component fluid systems, at least if the constituent atoms are electrically neutral. (Amorphous and polycrystalline solids of neutral atoms are other examples of systems with short-range correlation functions, to which the treatment of this subsection applies.) For such systems we shall cast the correlation terms F^C (74) and Ψ^C (90) in the momentum and energy equations in a convenient form.

In normal fluids the correlation function becomes negligible for s greater than the so-called 'correlation length'. This correlation length is much smaller than the distances over which the macroscopic quantities change appreciably. Then the correlation function may be approximated by the first two terms of a Taylor expansion

$$c_2(R, 1, R-s, 2; t) = c_2(R+\frac{1}{2}s, 1, R-\frac{1}{2}s, 2; t)$$

$$-\frac{1}{2}s \cdot \nabla c_2(R+\frac{1}{2}s, 1, R-\frac{1}{2}s, 2; t), \quad (102)$$

the Irving–Kirkwood approximation[1].

For a fluid of neutral atoms the correlation term F^C (74) in the *momentum equation* becomes then a divergence, because the first term at the right-hand side of (102) gives no contribution. In fact (74) with this first term vanishes owing to the trivial symmetry of $c_2(R+\frac{1}{2}s, 1, R-\frac{1}{2}s, 2; t)$ with respect to an interchange of the first and second pairs of arguments. In this way one gets

$$F^C = -\nabla \cdot \mathbf{P}^C \quad (103)$$

with the correlation pressure given by

$$\mathbf{P}^C \equiv -\int \sum_{n,m=1}^{\infty} (-1)^m \left(s\nabla_s \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right)$$

$$c_2(R+\frac{1}{2}s, 1, R-\frac{1}{2}s, 2; t) \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2. \quad (104)$$

The momentum equation for a fluid of neutral atoms is obtained from (62) with (72), (93) and (103). It reads finally

$$\frac{\partial \varrho v}{\partial t} = -\nabla \cdot (\varrho vv + \mathbf{P}) + F, \quad (105)$$

where the force density is

$$F = (\nabla E) \cdot P + (\nabla B) \cdot M + c^{-1} \frac{\partial}{\partial t}(P \wedge B) + c^{-1} \nabla \cdot (vP \wedge B) \quad (106)$$

[1] J. H. Irving and J. G. Kirkwood, op. cit.

(for systems of neutral atoms ϱ^e and J vanish) and the pressure tensor

$$\mathbf{P} = \mathbf{P}^K + \mathbf{P}^F + \mathbf{P}^S + \mathbf{P}^C. \tag{107}$$

The momentum equation (105) has the form of a *balance equation*, not of a conservation law. Indeed the momentum density ϱv does not only change as a consequence of momentum flow $\varrho v v + \mathbf{P}$, but also as a consequence of momentum 'production' F. The latter source term arises because the system is not closed. It vanishes if the electromagnetic fields are not present. (The expression (106) contains a time derivative and a divergence of quantities which might be grouped with the momentum density and the momentum flow respectively. This has not been done in order to keep together terms which depend exclusively on the Maxwell fields E, B, the polarizations P, M and the velocity v.)

The momentum flow of which (minus) the divergence appears in (105) consists of a convection part $(\varrho v v)$ together with the pressure tensor ($\mathbf{P}$). The latter quantity contains the kinetic pressure tensor $\mathbf{P}^K$ (63), a term $\mathbf{P}^F$ (73) with the magnetic field B and the potential pressure tensor $\mathbf{P}^S + \mathbf{P}^C$, where $\mathbf{P}^S$ (94) (with the atomic charge $\bar{\mu}_1^{(0)} = \bar{\mu}_2^{(0)} = 0$) contains a short range interatomic interaction multiplied by a distribution function f_2 with a long range, whereas $\mathbf{P}^C$ (104) contains the long range part of the interatomic interaction multiplied by a correlation function c_2 of short range. (The second term in the short range pressure $\mathbf{P}^S$ (94) has the same structure as the correlation pressure $\mathbf{P}^C$ (104). Their sum might, according to (7), be written with a product of one-point distribution functions. However, the way in which the potential pressure tensor $\mathbf{P}^S + \mathbf{P}^C$ has been written here has the advantage, as stated above, that the short-range character, of both contributions separately, is explicitly apparent.)

Furthermore the momentum balance equation (105) contains as a source term the force density F (106) exerted by the field (E, B) on a medium with polarizations (P, M). It includes the Kelvin force $(\nabla E) \cdot P$ on an electrically polarized medium and three force terms of magnetic origin: the first of these, $(\nabla B) \cdot M$, is analogous to the Kelvin force while the other two describe a coupling of the magnetic field and the electric polarization[1].

The momentum equation (105) may be written in the form of a *conservation law* by using the identity

[1] Part of these results were obtained already by H. A. Lorentz, Enc. Math. Wiss. V 2, fasc. 1 (Teubner, Leipzig 1904)200; A. Einstein and J. Laub, Ann. Physik **26**(1908)541; W. Dällenbach, Phys. Z. **27**(1926)632; P. Mazur and S. R. de Groot, Physica **22**(1956) 657; A. N. Kaufman, Phys. Fluids **8**(1965)935.

$$(\nabla E) \cdot P + (\nabla B) \cdot M = \nabla \cdot \{DE + BH - (\tfrac{1}{2}E^2 + \tfrac{1}{2}B^2 - M \cdot B)\mathbf{U}\} - c^{-1} \frac{\partial}{\partial t}(D \wedge B), \tag{108}$$

which follows from the Maxwell equations (13) with (14) for systems of neutral atoms ($\mathbf{U}$ is the unit tensor). Substituting this identity into (106) and the result into (105) one obtains

$$\frac{\partial(\varrho v + c^{-1} E \wedge B)}{\partial t}$$

$$= -\nabla \cdot \{\varrho v v + \mathbf{P} - DE - BH - c^{-1} v P \wedge B + (\tfrac{1}{2}E^2 + \tfrac{1}{2}B^2 - M \cdot B)\mathbf{U}\}. \tag{109}$$

This equation forms the conservation law of total momentum for a fluid of neutral atoms in an electromagnetic field. Both the momentum density and the momentum flow consist of a material part and a field part.

The correlation term Ψ^C (90), which plays a role in the *energy equation*, may likewise be written in a special form for fluid systems of neutral atoms. Since for such systems the approximation (102), which has the same structure as (92), is valid, one may follow the same procedure as in subsection *e*. In this way one obtains (cf. (101))

$$\Psi^C = -\nabla \cdot (v \varrho u^C + \mathbf{P}^C \cdot v + J_q^C) - \frac{\partial \varrho u^C}{\partial t}, \tag{110}$$

where

$$\varrho u^C \equiv \int \sum_{n,m=1}^{\infty} (-1)^m \left(\bar{\mu}_1^{(n)} : \nabla_s^n \bar{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right)$$

$$c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t)\,ds\,d1\,d2 \tag{111}$$

and

$$J_q^C \equiv -\int \sum_{n,m=1}^{\infty} (-1)^m \left[\{(s\hat{v}_1 \cdot \nabla_s - \hat{v}_1)\bar{\mu}_1^{(n)} : \nabla_s^n + s\dot{\bar{\mu}}_1^{(n)} : \nabla_s^n\} \bar{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right]$$

$$c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t)\,ds\,d1\,d2 \tag{112}$$

are the correlation contributions to the internal energy density and the heat flow. The energy equation for a fluid of neutral atoms is obtained from (80) with (88), (101) and (110). It reads finally:

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho v^2 + \varrho u) = -\nabla \cdot \{v(\tfrac{1}{2}\varrho v^2 + \varrho u) + \mathbf{P} \cdot v + J_q\} + \Psi, \tag{113}$$

where the 'power' density is ($J = 0$ for systems of neutral atoms)

$$\Psi \equiv \frac{\partial P}{\partial t} \cdot E + \nabla \cdot (v P \cdot E) - M \cdot \frac{\partial B}{\partial t}, \tag{114}$$

the specific internal energy

$$u \equiv u^{K} + u^{S} + u^{C}, \tag{115}$$

and the heat flow

$$J_q \equiv J_q^{K} + J_q^{F} + J_q^{S} + J_q^{C}. \tag{116}$$

The energy equation (113) has the form of a balance equation. It shows that the sum of the bulk kinetic energy density $\frac{1}{2}\varrho v^2$ and the internal energy density ϱu changes as a consequence of two causes: through the divergence of an energy flow and through a source term. The specific internal energy (115) consists of three parts. In the first place a contribution u^{K} (78) formed with the help of one-point distribution functions occurs. It consists of the energy due to atomic velocity fluctuations and the total intra-atomic energy. It will be referred to as the kinetic part of the specific internal energy. Furthermore two contributions u^{S} (97) (with the atomic charge $\bar\mu_1^{(0)} = \bar\mu_2^{(0)} = 0$) and u^{C} (111) with two-point distribution functions arise; these terms, which are due to interatomic forces, will be called together the potential part of the specific internal energy.

The energy flow in (113) contains besides convection terms with the local velocity v, the heat flow J_q (116). The latter consists of a kinetic part J_q^{K} (81), a part J_q^{F} (89), due to the action of the fields on the electric dipoles, and two terms J_q^{S} ($\equiv J_q^{S'} + J_q^{S''}$, v. (96) and (100) with $\bar\mu_1^{(0)} = \bar\mu_2^{(0)} = 0$) and J^{C} (112), which form together the potential part of the heat flow. (Just as in the potential pressure tensor one could have combined here part of the short range internal energy with the correlation energy in such a way that a product of two one-point distribution functions occurs. The same remark applies to the potential part of the heat flow.)

The power density Ψ (114) contains two terms with time derivatives, showing the same asymmetry as was present in the atomic energy equation. This asymmetry will play a role in the first law of thermodynamics, as will be shown in section 7. Furthermore the power density Ψ contains a divergence of a vector which might be shifted to the energy flow. We have preferred to keep it together with the other terms containing the macroscopic Maxwell fields E, B, P and M.

The balance equation (113) may be transformed into a conservation law. In fact from Maxwell's equations it follows for neutral and current-free

systems that:

$$\frac{\partial P}{\partial t} \cdot E - M \cdot \frac{\partial B}{\partial t} = -c\nabla \cdot (E \wedge H) - \frac{1}{2} \frac{\partial}{\partial t} (E^2 + B^2). \tag{117}$$

If this is inserted in (113–114) one gets

$$\frac{\partial}{\partial t} (\tfrac{1}{2}\varrho v^2 + \varrho u + \tfrac{1}{2}E^2 + \tfrac{1}{2}B^2)$$
$$= -\nabla \cdot \{v(\tfrac{1}{2}\varrho v^2 + \varrho u) + \mathbf{P} \cdot v + J_q + cE \wedge H - vP \cdot E\}, \tag{118}$$

which expresses the conservation of total energy for a fluid system of neutral atoms. Both the energy density and the energy flow consist of a material part and a field part. The latter includes the Poynting vector.

The right-hand sides of the conservation laws (109) and (118) of momentum and energy contain the total momentum flow and the total energy flow respectively. Since only the divergences of these quantities play a role, they are determined up to a divergence-free part. The expressions given are thus not uniquely fixed, although they appear to be the simplest ones[1].

g. *Mixtures, in particular plasmas*

In the preceding the treatment was confined to one-component systems. The extension to mixtures of several components is straightforward. In that case one has to introduce distribution functions for each separate species. The one-point distribution function $f_1^a(1; t)$ carries an extra label a which indicates the species. Now $f_1^a(1; t)d1$ is the probability, normalized to N^a (the number of atoms of species a), to find an atom of species a with parameters in the range d1 in fluxion space. Similarly the two-point distribution function is defined in such a way that $f_2^{ab}(1, 2; t)d1\,d2$ is the joint probability, normalized to $N^a N^b$ (if $a \neq b$) or $N^a(N^a - 1)$ (if $a = b$), to find an atom of species a in the range d1 and an atom of species b in the range d2. The correlation function $c_2^{ab}(1, 2; t)$ is now defined as the difference $f_2^{ab}(1, 2; t) - f_1^a(1; t)f_1^b(2; t)$.

A case in which the use of this kind of distribution functions is essential is a plasma consisting of a mixture of oppositely charged ions and electrons, of which the internal structure is supposed to play no role. For such a plasma

[1] Much discussion has been devoted to this point, in particular with respect to the Poynting vector: v. G. H. Livens, Phil. Mag. **34**(1917)385; C. O. Hines, Canad. J. Phys. **30**(1952) 123; F. Bopp, Ann. Physik **11**(1963)35; E. M. Pugh and G. E. Pugh, Am. J. Phys. **35**(1967) 153; L. W. Zelby, Am. J. Phys. **35**(1967)1094; W. Shockley, Phys. Lett. **28A**(1968)185.

the macroscopic mass density is

$$\varrho(R, t) = \sum_a m_a f_1^a(R; t), \tag{119}$$

and the local barycentric velocity is defined by

$$\varrho(R, t)v(R, t) = \sum_a \int m_a v_1 f_1^a(R, v_1; t)dv_1 . \tag{120}$$

They satisfy the macroscopic law of mass conservation (59). The *momentum* law that follows from the atomic equation (I.50) reads (cf. (62)) in the case of the plasma

$$\frac{\partial \varrho v}{\partial t} = -\nabla \cdot (\varrho vv + \mathbf{P}^K) + F^L, \tag{121}$$

where the kinetic pressure is now (cf. (63))

$$\mathbf{P}^K \equiv \sum_a \int m_a \hat{v}_1 \hat{v}_1 f_1^a(R, v_1; t)dv_1 \tag{122}$$

with the velocity fluctuation given by (61). Furthermore the force density is (cf. (72))

$$F^L = \varrho^e E + c^{-1} J \wedge B + F^C, \tag{123}$$

where the macroscopic charge and current densities are (18) or alternatively (19):

$$\varrho^c(R, t) = \sum_a e_a f_1^a(R, t), \qquad J(R, t) = \sum_a \int e_a v_1 f_1^a(R, v_1; t)dv_1 \tag{124}$$

and the correlation force density (cf. (74))

$$F^C = -\sum_{a,b} \int \left(\nabla_s \frac{e_a e_b}{4\pi s}\right) c_2^{ab}(R, R-s; t)ds. \tag{125}$$

(The terms (73) and (75) are absent in (123) and (121) respectively because the internal structure of the charged particles has been ignored here.)

Let us now consider the correlation force F^C for the special case of a plasma in which the correlation function vanishes rapidly if the interparticle distance becomes of macroscopic order. This is the case for plasmas without space charge and sufficiently near equilibrium, as a result of Debye shielding[1]. Then using the Irving–Kirkwood approximation (102) we may write (125)

[1] A. N. Kaufman, Phys. Fluids 6(1963)1574, who gives a treatment similar to that of this subsection.

as a divergence:

$$F^C = -\nabla \cdot \mathbf{P}^C \tag{126}$$

with the correlation pressure

$$\mathbf{P}^C = -\sum_{a,b} \int \left(s\nabla_s \frac{e_a e_b}{8\pi s}\right) c_2^{ab}(R+\tfrac{1}{2}s, R-\tfrac{1}{2}s; t)ds. \tag{127}$$

The momentum equation (121) may now be written as

$$\frac{\partial \varrho v}{\partial t} = -\nabla \cdot (\varrho vv + \mathbf{P}) + c^{-1} J \wedge B, \tag{128}$$

where the total pressure is the sum of the kinetic and the correlation pressure

$$\mathbf{P} = \mathbf{P}^K + \mathbf{P}^C \tag{129}$$

and where the last term of (128) is the Lorentz force in a neutral medium.

The *energy* law that follows for the plasma from the atomic equation (I.63) is (cf. (80))

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho v^2 + \varrho u^K) = -\nabla \cdot \{v(\tfrac{1}{2}\varrho v^2 + \varrho u^K) + \mathbf{P}^K \cdot v + J_q^K\} + \varPsi^L, \tag{130}$$

where the kinetic part of the internal energy density is given by (cf. (78))

$$\varrho u^K = \sum_a \int \tfrac{1}{2} m_a \hat{v}_1^2 f_1^a(R, v_1; t)dv_1 , \tag{131}$$

and the kinetic part of the heat flow by (cf. (81))

$$J_q^K = \sum_a \int \hat{v}_1 \tfrac{1}{2} m_a \hat{v}_1^2 f_1^a(R, v_1; t)dv_1 . \tag{132}$$

Furthermore the power density is here (cf. (88))

$$\varPsi^L = J \cdot E + \varPsi^C \tag{133}$$

with the current density J (124) and the correlation contribution (cf. (90))

$$\varPsi^C = -\sum_{a,b} \int \left(v_1 \cdot \nabla_s \frac{e_a e_b}{4\pi s}\right) c_2^{ab}(R, v_1, R-s; t)ds\, dv_1 . \tag{134}$$

(The terms (89) and (91) are absent from (133) and (130) respectively because the charged particles have no internal structure.) For a sufficiently homogeneous plasma without space charge ($\varrho^c = 0$) we apply the Irving–Kirkwood approximation (102) on the correlation power density (134):

$$\Psi^C = -\sum_{a,b} \int v_1 \cdot \nabla_s \frac{e_a e_b}{4\pi s} c_2^{ab}(R + \tfrac{1}{2}s, v_1, R - \tfrac{1}{2}s; t) ds\, dv_1$$

$$+ \nabla \cdot \sum_{a,b} \int s v_1 \cdot \nabla_s \frac{e_a e_b}{8\pi s} c_2^{ab}(R + \tfrac{1}{2}s, v_1, R - \tfrac{1}{2}s; t) ds\, dv_1. \quad (135)$$

The first term at the right-hand side may be transformed to the sum of a time derivative and a divergence, since as a consequence of the conservation of probability in fluxion space one has

$$\sum_{a,b} \frac{\partial}{\partial t} \int \frac{e_a e_b}{8\pi s} c_2^{ab}(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s; t) ds$$

$$= -\nabla \cdot \sum_{a,b} \int (v_1 + v_2) \frac{e_a e_b}{16\pi s} c_2^{ab}(R + \tfrac{1}{2}s, v_1, R - \tfrac{1}{2}s, v_2; t) ds\, dv_1\, dv_2$$

$$+ \sum_{a,b} \int (v_1 - v_2) \cdot \nabla_s \frac{e_a e_b}{8\pi s} c_2^{ab}(R + \tfrac{1}{2}s, v_1, R - \tfrac{1}{2}s, v_2; t) ds\, dv_1\, dv_2 \quad (136)$$

(where in the last term a partial integration has been performed). Owing to the symmetry of the correlation function the last term is equal to minus the first term at the right-hand side in (135). This allows us to write (135) in the form (cf. (110))

$$\Psi^C = -\nabla \cdot (v \varrho u^C + \mathbf{P}^C \cdot v + J_q^C) - \frac{\partial \varrho u^C}{\partial t}, \quad (137)$$

where now the correlation part of the internal energy density is

$$\varrho u^C = \sum_{a,b} \int \frac{e_a e_b}{8\pi s} c_2^{ab}(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s; t) ds, \quad (138)$$

and the correlation part of the heat flow

$$J_q^C = \sum_{a,b} \int \left\{ (\hat{v}_1 - s \hat{v}_1 \cdot \nabla_s) \frac{e_a e_b}{8\pi s} \right\} c_2(R + \tfrac{1}{2}s, v_1, R - \tfrac{1}{2}s; t) ds\, dv_1. \quad (139)$$

The energy equation follows if (133) with (137) is substituted into (130):

$$\frac{\partial}{\partial t} \left(\tfrac{1}{2}\varrho v^2 + \varrho u \right) = -\nabla \cdot \{ v(\tfrac{1}{2}\varrho v^2 + \varrho u) + \mathbf{P} \cdot v + J_q \} + J \cdot E, \quad (140)$$

where the total internal specific energy

$$u = u^K + u^C \quad (141)$$

is the sum of a kinetic part, given in (131), and a correlation part, given in

(138). Furthermore the total pressure **P** has been given in (129) and the total heat flow

$$J_q = J_q^K + J_q^C \quad (142)$$

is again the sum of a kinetic part (132) and a correlation part (139). The source term in (140) is the well-known electric power density.

One may write both the momentum law (128) and the energy law (140) in the form of conservation laws, if one uses the identities

$$c^{-1} J \wedge B = \nabla \cdot \{ EE + BB - \tfrac{1}{2}(E^2 + B^2)U \} - c^{-1} \frac{\partial}{\partial t}(E \wedge B) \quad (143)$$

and

$$J \cdot E = -c \nabla \cdot (E \wedge B) - \frac{1}{2} \frac{\partial}{\partial t}(E^2 + B^2) \quad (144)$$

respectively, which both follow directly from Maxwell's equations for a neutral unpolarized medium ($\varrho^e = 0$, $P = 0$, $M = 0$). One obtains in this way

$$\frac{\partial}{\partial t} \left(\varrho v + c^{-1} E \wedge B \right) = -\nabla \cdot \{ \varrho vv + \mathbf{P} - EE - BB + \tfrac{1}{2}(E^2 + B^2)U \} \quad (145)$$

for the conservation of total momentum, and

$$\frac{\partial}{\partial t} \left(\tfrac{1}{2}\varrho v^2 + \varrho u + \tfrac{1}{2}E^2 + \tfrac{1}{2}B^2 \right) = -\nabla \cdot \{ v(\tfrac{1}{2}\varrho v^2 + \varrho u) + \mathbf{P} \cdot v + J_q + cE \wedge B \} \quad (146)$$

for the conservation of total energy.

h. *Crystalline solids*

Up to subsection *e* the derivations were independent of the nature of the systems, provided that these were sufficiently uniform. The latter restriction was made in order to write the short range terms in the momentum and energy equations in convenient form. In subsections *f* and *g*, where the correlation terms were discussed, it was necessary to specify the system further: we confined ourselves to fluids of neutral atoms (and amorphous or polycrystalline solids) and to neutral plasmas, for which the correlation function is of short range. Then the Irving–Kirkwood approximation could be employed.

In this subsection we shall study systems with correlation functions of arbitrary range, such as crystalline solids. Even then it is possible to trans-

form the correlation terms to a divergence, or to a divergence and a time derivative. This may be done with the help of the following artifice[1]. Let us write the following identity for the correlation function of a one-component system[2]

$$c_2(R, 1, R-s, 2; t) - c_2(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)$$

$$= -\int_{-1}^{0} \frac{\partial}{\partial\lambda} c_2\{R+\tfrac{1}{2}(\lambda+1)s, 1, R+\tfrac{1}{2}(\lambda-1)s, 2; t\}d\lambda. \quad (147)$$

Since the correlation function in the integrand depends on position coordinates which are combinations of $R+\tfrac{1}{2}\lambda s$ and $\tfrac{1}{2}s$ one may replace the operator $\partial/\partial\lambda$ by $\tfrac{1}{2}s\cdot\nabla$. In this way one obtains for (147):

$$c_2(R, 1, R-s, 2; t)$$
$$= c_2(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t) - \tfrac{1}{2}s\cdot\nabla c_2^+(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t), \quad (148)$$

with the 'mean correlation function':

$$c_2^+(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t) \equiv \int_{-1}^{0} c_2\{R+\tfrac{1}{2}(\lambda+1)s, 1, R+\tfrac{1}{2}(\lambda-1)s, 2; t\}d\lambda.$$

$$(149)$$

(If c_2 vanishes rapidly with increasing interatomic distance $|s|$ so that a correlation length exists, and if moreover c_2 changes slowly if both positions are shifted over a distance of the order of the correlation length one may consider the integrand in (149) as a constant. Choosing its value at $\lambda = 0$ the 'mean correlation function' c_2^+ reduces then to the ordinary correlation function c_2. In this case (148) reduces to the Irving–Kirkwood approximation (102).)

Using (148) which has the same form as (102) we may find expressions for the correlation terms in the momentum and energy laws for systems with long range correlations. These are in form very similar to the expressions valid for fluids. In fact for the case of long range order the momentum balance becomes

$$\frac{\partial \varrho v}{\partial t} = -\nabla\cdot(\varrho vv+P)+\varrho^e E+c^{-1}J\wedge B+(\nabla E)\cdot P+(\nabla B)\cdot M$$

$$+c^{-1}\frac{\partial}{\partial t}(P\wedge B)+c^{-1}\nabla\cdot(vP\wedge B) \quad (150)$$

[1] J. H. Irving and J. G. Kirkwood, op. cit.
[2] If the system is a mixture one should add indices a and b to the distribution functions and the atomic parameters such as the charges and the masses. Furthermore summations over a and b are then to be added.

with a pressure tensor P that consists of four contributions (cf. (107)), viz P^K (63), P^F (73), P^S (94) and the correlation pressure P^C given by (cf. (104)):

$$P^C \equiv -\int \sum_{n,m=0}^{\infty} (-1)^m \left(sV_s\, \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s}\right)$$
$$c_2^+(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)ds\,d1\,d2. \quad (151)$$

Likewise the energy balance equation for the case of long range order gets the form

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho v^2+\varrho u) = -\nabla\cdot\{v(\tfrac{1}{2}\varrho v^2+\varrho u)+P\cdot v+J_q\}$$
$$+J\cdot E+\frac{\partial P}{\partial t}\cdot E+\nabla\cdot(vP\cdot E)-M\cdot\frac{\partial B}{\partial t}, \quad (152)$$

with a specific internal energy u that consists of three parts (cf. (115)), viz u^K (78), u^S (97) and the correlation contribution u^C given by (cf. (111))

$$\varrho u^C \equiv \int \sum_{n,m=0}^{\infty} (-1)^m \left(\overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s}\right)$$
$$c_2(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)ds\,d1\,d2. \quad (153)$$

Furthermore the heat flow consists of four parts (cf. (116)), viz J_q^K (81), J_q^F (89), J_q^S (96), (100) and the correlation contribution given by (cf. (112))

$$J_q^C \equiv -\int s \sum_{n,m=0}^{\infty} (-1)^m \left\{(\hat{v}_1\cdot\nabla_s\overline{\mu}_1^{(n)} : \nabla_s^n + \dot{\underline{\mu}}_1^{(n)} : \nabla_s^n)\overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s}\right\}$$
$$c_2^+(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)ds\,d1\,d2$$

$$+\int \hat{v}_1 \sum_{n,m=0}^{\infty} (-1)^m \left(\overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s}\right)$$
$$c_2(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)ds\,d1\,d2, \quad (154)$$

where only in the first part the 'mean correlation function' occurs.

Finally it should be remarked that the procedure employed to write the correlation terms in the form of a divergence (or a divergence and a time derivative) is not unique. However, the statistical expressions obtained have been preferred because of their formal resemblance to the corresponding expressions for fluid systems.

i. *Galilean invariance*

In the preceding non-relativistic balance equations of momentum and energy have been obtained. We shall investigate whether they are indeed covariant with respect to the Galilei group. The rotational invariance of all equations is manifest since they have been formulated in tensor notation. The transformation character with respect to a pure Galilean transformation (22) needs to be considered in some detail.

Let us first show that the conservation law of mass (59) possesses Galilean covariance. Indeed the mass density defined in (56) is an invariant

$$\varrho'(R', t') = \varrho(R, t), \tag{155}$$

as follows from the invariance of the one-point distribution function (cf. (24)):

$$f_1'(1'; t') = f_1(1; t), \tag{156}$$

where 1 stands for the position, velocity etc. of atom 1; primes indicate the corresponding transformed quantities. Furthermore it follows from (58) with (155) and (156) that

$$v'(R', t') = v(R, t) + V. \tag{157}$$

Now from (23), (155) and (157) one proves immediately that (59) is a covariant equation, i.e. also valid with primes.

We now turn to the momentum balance (105–106) for fluid systems of neutral atoms. With the help of the mass conservation law (59) it may be brought into the form

$$\varrho \frac{dv}{dt} = -\nabla \cdot P + (\nabla E) \cdot P + (\nabla B) \cdot M + c^{-1} \varrho \frac{d}{dt}(vP \wedge B), \tag{158}$$

where $v \equiv \varrho^{-1}$ is the specific volume and

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + v \cdot \nabla, \tag{159}$$

the material time derivative. By inspection of the expression (107) with (63), (73), (94) and (104) it follows from (27), (61) and the invariance of the distribution function expressed by (156) and

$$f_2'(1', 2'; t') = f_2(1, 2; t),$$
$$c_2'(1', 2'; t') = c_2(1, 2; t), \tag{160}$$

that the pressure P is invariant with respect to pure Galilean transformations:

$$P'(R', t') = P(R, t). \tag{161}$$

Hence, according to (23), the term $\nabla \cdot P$ in the momentum equation (158) is invariant with respect to pure Galilean transformations. The other terms in (158), viz $\varrho \, dv/dt$, $(\nabla E) \cdot P + (\nabla B) \cdot M$ and $c^{-1}\varrho(d/dt)(vP \wedge B)$ are also, separately, invariant under pure Galilean transformations as follows from (23), (26), (27), (155), (157) and (159), where terms of order c^{-2} must of course be discarded. In this way the Galilean covariance of the momentum balance has been proved for the case of fluids systems of neutral atoms. The momentum balance for neutral plasmas and for systems with long range correlations (subsections g and h) also possess Galilean covariance as follows by a similar reasoning from the transformation formulae.

Let us discuss now the Galilean covariance of the energy balance equation (113) for fluids of neutral atoms. With the help of the mass conservation law (59) and the material time derivative (159) it may be written as

$$\varrho \frac{d}{dt}\left(\tfrac{1}{2}v^2 + u\right) = -\nabla \cdot (P \cdot v + J_q)$$
$$+ \varrho \frac{d(vP)}{dt} \cdot E - M \cdot \frac{dB}{dt} + v \cdot \{(\nabla E) \cdot P + (\nabla B) \cdot M\}. \tag{162}$$

If the first term is rewritten with the help of the (Galilei covariant) momentum equation (158) we obtain

$$\varrho \frac{du}{dt} = -\nabla \cdot J_q - \tilde{P} : (\nabla v)$$
$$+ \varrho \frac{d(vP)}{dt} \cdot (E + c^{-1}v \wedge B) - (M + c^{-1}v \wedge P) \cdot \frac{dB}{dt}, \tag{163}$$

where $\tilde{P}$ is the transposed of the tensor P (or $\tilde{P}_{ij} = P_{ji}$) and the double dot indicates a double contraction of two tensors $(A : B \equiv \sum_{i,j} A_{ij} B_{ji})$. With (61), (155), (156), (157) and (160) it follows by inspection that the contributions (78), (97) and (111) to the specific internal energy u (115) are each Galilei invariant, so that

$$u'(R', t') = u(R, t). \tag{164}$$

Consequently with (23), (155) and (159) it follows that the left-hand side of (163) is invariant. Furthermore with the help of (27), (61), (156), (157) and (160) it is seen that the contributions (81), (89), (96), (100) and (112) to the

heat flow J_q (116) are each Galilei invariant, so that

$$J_q'(R', t') = J_q(R, t). \tag{165}$$

Hence the invariance of the first term at the right-hand side of (163) follows if (23) is used. The invariance of the second term at the right-hand side of (163) follows from (23), (157) and (161). Finally if one uses (23), (26), (27), (155) and (157) one may prove the invariance of each of the last two terms of (163). In this way the Galilean covariance of equation (163) has been established, and hence that of the energy equation (162). We have chosen to give this proof via equation (163) because, in contrast with (162), all its terms are separately invariant. For (neutral) plasmas and for systems with long range correlations the Galilean covariance of the energy equations is proved in an analogous way.

6   The angular momentum equations

a. The inner angular momentum balance

On a par with the momentum and energy equations derived in the preceding section, macroscopic angular momentum laws will now be obtained by averaging the corresponding atomic equations. The macroscopic angular momentum density is defined as the average:

$$S(R, t) = \langle \sum_k \bar{s}_k \delta(R_k - R) \rangle, \tag{166}$$

where $\bar{s}_k$ is the inner angular momentum (I.68) of atom k. The time derivative of $S(R, t)$ is found with the help of the lemma (2) and (I.76):

$$\frac{\partial S}{\partial t} = -\nabla \cdot \langle \sum_k v_k \bar{s}_k \delta(R_k - R) \rangle + \langle \sum_k (d_k^L + d_k^S) \delta(R_k - R) \rangle. \tag{167}$$

Introducing the velocity fluctuation $\hat{v}_k$ (61) we get

$$\frac{\partial S}{\partial t} = -\nabla \cdot (vS + J_s^K) + D^L + D^{S*} \tag{168}$$

with the kinetic flow of inner angular momentum

$$J_s^K = \int \hat{v}_1 \bar{s}_1 f_1(R, v_1, \bar{s}_1; t) dv_1 d\bar{s}_1 \tag{169}$$

and the abbreviations $D^{L,S*} = \langle \sum_k d_k^{L,S} \delta(R_k - R) \rangle$ with $d_k^{L,S}$ given by (I.77-78).

Let us first consider the external field part D_e^L of D^L. It may be written with the help of the polarizations (65), if one uses the vector identity $a \wedge (b \wedge c) + \text{cycl.} = 0$:

$$D_e^L = P \wedge E_e + M \wedge B_e + c^{-1} v \wedge (P \wedge B_e)$$
$$+ c^{-1} \int \hat{v}_1 \wedge (\bar{\mu}_1^{(1)} \wedge B_e) f_1(R, v_1, \bar{\mu}_1^{(1)}; t) dv_1 d\bar{\mu}_1^{(1)}. \tag{170}$$

The part of the long range term in (168) that is due to the interatomic interactions is

$$D^L - D_e^L = \int \left(\sum_{n,m=0}^{\infty} n \nabla_1 \wedge \bar{\mu}_1^{(n)} : \nabla_1^{n-1} \bar{\mu}_2^{(m)} : \nabla_2^m \frac{1}{4\pi |R_1 - R_2|} \right)$$
$$\delta(R - R_1) f_2(R_1, 1, R_2, 2; t) dR_1 dR_2 d1 d2, \tag{171}$$

where 1 and 2 indicate all electric multipole moments. We split this expression with the help of (7). In the uncorrelated part we introduce the macroscopic charge and polarization densities (64) and (65), omitting (just as in § 5c) higher multipole moments. In this way (171) becomes

$$D^L - D_e^L = -\int P(R, t) \wedge \nabla \{ \varrho^e(R', t) + P(R', t) \cdot \nabla' \} \frac{1}{4\pi |R - R'|} dR'$$
$$+ \int \left(\sum_{n,m=0}^{\infty} n \nabla \wedge \bar{\mu}_1^{(n)} : \nabla^{n-1} \bar{\mu}_2^{(m)} : \nabla'^m \frac{1}{4\pi |R - R'|} \right)$$
$$c_2(R, 1, R', 2; t) dR' d1 d2. \tag{172}$$

The total long range moment density which is given by the sum of (170) and (171) may be written with the help of (71) as

$$D^L = P \wedge E + M \wedge B + c^{-1} v \wedge (P \wedge B) + D^F + D^{C*}, \tag{173}$$

where the last two contributions are given by

$$D^F \equiv c^{-1} \int \hat{v}_1 \wedge (\bar{\mu}_1^{(1)} \wedge B) f_1(R, v_1, \bar{\mu}_1^{(1)}; t) dv_1 d\bar{\mu}_1^{(1)}, \tag{174}$$

$$D^{C*} \equiv \int d^C(s, 1, 2) c_2(R, 1, R-s, 2; t) ds d1 d2, \tag{175}$$

with the abbreviation

$$d^C(s, 1, 2) \equiv \sum_{n,m=0}^{\infty} (-1)^m n \nabla_s \wedge \bar{\mu}_1^{(n)} : \nabla_s^{n-1} \bar{\mu}_2^{(m)} : \nabla_s^m \frac{1}{4\pi s}. \tag{176}$$

Finally the short range moment in (168) reads

$$D^{S*} = \int d^S(s, 1, 2) f_2(R, 1, R-s, 2; t) ds \, d1 \, d2 \qquad (177)$$

with the abbreviation

$$d^S(s, 1, 2) \equiv \int \left\{ - \sum_{i,j} r_{1i} \wedge \nabla_s \frac{e_i e_j}{4\pi |s + r_{1i} - r_{2j}|} - d^C(s, 1, 2) \right\} \\ f_2(R, 1, R-s, 2; t) ds \, d1 \, d2. \qquad (178)$$

The integrand in (177) vanishes if the atoms are outside each other. Since the two-point distribution function remains practically unchanged if both R and $R-s$ are shifted over a distance of the order of an atomic diameter, one may write the short range moment (177) with the help of (92) as

$$D^{S*} = -\nabla \cdot J_s^S + D^S, \qquad (179)$$

with the short range contribution to the inner angular momentum flow

$$J_s^S \equiv \int \tfrac{1}{2} s d^S(s, 1, 2) f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) ds \, d1 \, d2, \qquad (180)$$

and the source term:

$$D^S \equiv \int d^S(s, 1, 2) f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) ds \, d1 \, d2. \qquad (181)$$

The correlation contribution D^{C*} will be specified for particular systems in the next subsections.

b. *Fluid systems*

For fluid systems of neutral atoms (and amorphous or polycrystalline solids) the correlation function has usually short range. In that case it may be expanded as in (102). In that way the correlation contribution D^{C*} (175) gets the form

$$D^{C*} = -\nabla \cdot J_s^C + D^C \qquad (182)$$

with the correlation contribution to the inner angular momentum flow:

$$J_s^C \equiv \int \tfrac{1}{2} s d^C(s, 1, 2) c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) ds \, d1 \, d2 \qquad (183)$$

and the source term

$$D^C \equiv \int d^C(s, 1, 2) c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) ds \, d1 \, d2, \qquad (184)$$

where $d^C(s, 1, 2)$ has been given by (176) (with the atomic charges $\bar{\mu}_1^{(0)} = \bar{\mu}_2^{(0)} = 0$).

The balance equation (168) of the inner angular momentum becomes, for fluid systems of neutral atoms, upon insertion of (173) and (179):

$$\frac{\partial S}{\partial t} = -\nabla \cdot (vS + J_s) + D_s + P \wedge E + M \wedge B + c^{-1} v \wedge (P \wedge B). \qquad (185)$$

The conduction flow of inner angular momentum consists of three parts:

$$J_s = J_s^K + J_s^S + J_s^C, \qquad (186)$$

where the various contributions have been given in (169), (180) and (183) with (176) and (178) (with the atomic charges $\bar{\mu}_1^{(0)} = \bar{\mu}_2^{(0)} = 0$). Furthermore the source term contains a material part

$$D_s = D^F + D^S + D^C, \qquad (187)$$

where the three contributions have been given in (174), (181) and (184) with (176) and (178) (again with $\bar{\mu}_1^{(0)} = \bar{\mu}_2^{(0)} = 0$). The other source terms are the torque densities which the Maxwell fields exert on the polarization densities in the moving fluid.

The source terms with the Maxwell fields may be written in a simpler form if 'rest frame quantities' are introduced. The rest frame (denoted by primes) is related to the observer's frame by a pure Galilean transformation (22) with transformation velocity $V = -v$, such that $v' = 0$ (cf. (157)). Then the Maxwell fields and polarizations transform according to (26) and (27) (up to order c^{-1}):

$$E' = E + c^{-1} v \wedge B, \qquad B' = B - c^{-1} v \wedge E,$$
$$P' = P, \qquad M' = M + c^{-1} v \wedge P. \qquad (188)$$

With the help of these formulae we get for the source term (up to order c^{-1})

$$P \wedge E + M \wedge B + c^{-1} v \wedge (P \wedge B) = P' \wedge E' + M' \wedge B'. \qquad (189)$$

In fluid systems quite often the rest frame polarizations P' and M' are parallel to the rest frame fields E' and B' respectively. In that case the field source terms (189) vanish.

The equation (185) is a balance equation: the inner angular momentum is not conserved. A conserved quantity is obtained if the orbital angular momentum

$$L(R, t) \equiv R \wedge (\varrho v + c^{-1} E \wedge B) \tag{190}$$

is added to it. The time derivative of the latter quantity may be obtained with the help of (109):

$$\frac{\partial L}{\partial t} = -\nabla \cdot (vL + \mathbf{J}_l) + P_A - D \wedge E - B \wedge H - c^{-1} v \wedge (P \wedge B). \tag{191}$$

Here the conduction flow of orbital angular momentum is

$$\mathbf{J}_l = -P \wedge R - D(R \wedge E) - B(R \wedge H) - c^{-1} vR \wedge (D \wedge B)$$
$$+ \boldsymbol{\epsilon} \cdot R(\tfrac{1}{2} E^2 + \tfrac{1}{2} B^2 - M \cdot B). \tag{192}$$

Furthermore $P_A \equiv \boldsymbol{\epsilon} : \tilde{P}$ is the antisymmetric part of the pressure tensor P ($\boldsymbol{\epsilon}$ is the Levi-Civita tensor with components ε^{ijk} so that the components of P_A are $P_A^i = \varepsilon^{ijk} P_{jk}$).

If (185) and (191) are added one obtains a conservation law for the total angular momentum density $S + L$, since the source terms cancel, as we shall now show. Indeed the source terms with fields in (185) and (191) cancel immediately if one uses the definitions $D = E + P$ and $H = B - M$. Furthermore the antisymmetric part of the pressure tensor follows from (107) with (63), (73), (94) and (104):

$$P_A = -c^{-1} \int \hat{v}_1 \wedge (\overline{\mu}_1^{(1)} \wedge B) f_1(R, 1; t) \mathrm{d}1$$

$$- \int \left\{ s \wedge \nabla_s \left(\sum_{i,j} \frac{e_i e_j}{8\pi |s + r_{1i} - r_{2j}|} - \sum_{n,m=1}^{\infty} (-1)^m \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right) \right\}$$
$$f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2$$

$$- \int \sum_{n,m=1}^{\infty} (-1)^m \left(s \wedge \nabla_s \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right)$$
$$c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2. \tag{193}$$

The first term at the right-hand side is equal to $-D^F$ (174). The second term may be transformed to

$$\int \left\{ \sum_{i,j} (r_{1i} - r_{2j}) \wedge \nabla_s \frac{e_i e_j}{8\pi |s + r_{1i} - r_{2j}|} \right.$$

$$- \sum_{n,m=1}^{\infty} (-1)^m n (\overline{\mu}_1^{(n)} : \nabla_s^{n-1}) \wedge \nabla_s \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s}$$

$$\left. - \sum_{n,m=1}^{\infty} (-1)^m m \overline{\mu}_1^{(n)} : \nabla_s^n (\overline{\mu}_2^{(m)} : \nabla_s^{m-1}) \wedge \nabla_s \frac{1}{8\pi s} \right\}$$
$$f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2; t) \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2. \tag{194}$$

Using the symmetry of the distribution function f_2 with respect to the interchange of 1 and 2 together with s and $-s$, we find that (194) is equal to $-D^S$ (181) with (178) and (176). In the same way one finds that the third term of (193) is equal to $-D^C$ (184) with (176). So finally the antisymmetric part (193) of the pressure tensor is equal to the material source term (187) of the inner angular momentum balance:

$$P_A = -D_s. \tag{195}$$

This allows one to write (185) in the alternative form:

$$\frac{\partial S}{\partial t} = -\nabla \cdot (vS + \mathbf{J}_s) - P_A + P \wedge E + M \wedge B + c^{-1} v \wedge (P \wedge B). \tag{196}$$

If we add equations (191) and (196) we have now

$$\frac{\partial (L + S)}{\partial t} = -\nabla \cdot \{v(L + S) + \mathbf{J}_l + \mathbf{J}_s\}, \tag{197}$$

which is the conservation law of total angular momentum $L + S$ for a fluid system of neutral atoms.

c. Plasmas

In plasmas the internal structure of the ions is usually disregarded. Then the inner angular momentum does not occur either. The angular momentum is thus entirely of orbital origin

$$L(R, t) \equiv R \wedge (\varrho v + c^{-1} E \wedge B). \tag{198}$$

From the conservation law (145) of total momentum for plasmas follows:

$$\frac{\partial L}{\partial t} = -\nabla \cdot (vL + \mathbf{J}_l), \tag{199}$$

where we used the symmetrical character of the material pressure tensor (129) with (122) and (127). Furthermore the flow of angular momentum is (cf. (192)):

$$\mathbf{J}_l = -P \wedge R - E(R \wedge E) - B(R \wedge B) - c^{-1} vR \wedge (E \wedge B) + \boldsymbol{\epsilon} \cdot R(\tfrac{1}{2} E^2 + \tfrac{1}{2} B^2) \tag{200}$$

(with $\boldsymbol{\epsilon}$ the Levi-Civita tensor). Hence as (199) shows the angular momentum satisfies a local conservation law.

d. *Crystalline solids*

In the preceding two subsections we studied systems with short range correlations. Now we shall turn to the general case of arbitrary range correlations – as occur in crystalline solids – including the effects due to charged atoms. Then all results of subsection *a* remain valid[1].

Since the correlation function is no longer of short range, the Irving-Kirkwood approximation (102) is not applicable. Nevertheless by use of an artifice of the type (148) we may still obtain a formula (182), such that again (195) is valid. Indeed with the help of the identity

$$c_2(R, 1, R-s, 2; t) = c_2^{\ddagger}(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s; t)-\tfrac{1}{2}s\cdot\nabla c_2^{\ddagger}(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s; t),$$
(201)

where

$$c_2^{\ddagger}(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t) \equiv \frac{1}{2}\int_{-1}^{+1} c_2\{R+\tfrac{1}{2}(\lambda+1)s, 1, R+\tfrac{1}{2}(\lambda-1)s, 2; t\}d\lambda$$
(202)

and

$$c_2^{\ddagger}(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)$$
$$\equiv \frac{1}{2}\int_{-1}^{+1}(1-\lambda)c_2\{R+\tfrac{1}{2}(\lambda+1)s, 1, R+\tfrac{1}{2}(\lambda-1)s, 2; t\}d\lambda,$$
(203)

one may write (cf. (182))

$$D^{C*} = -\nabla\cdot J_s^C + D^C.$$
(204)

Here the correlation part of the inner angular momentum flow is

$$J_s^C = \int \tfrac{1}{2}sd^C(s, 1, 2)c_2^{\ddagger}(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)ds\,d1\,d2,$$
(205)

while the source term is

$$D^C = \int d^C(s, 1, 2)c_2^{\ddagger}(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2; t)ds\,d1\,d2.$$
(206)

In these expressions $d^C(s, 1, 2)$ is given by (176).

Furthermore one may prove that just as in subsection *b*

$$D^C = -P_A^C,$$
(207)

where P_A^C is the antisymmetric part of the correlation pressure (151). Therefore also (195) is valid in the present case, and consequently (196) and (197).

[1] For mixtures an extra summation over the indices labelling the species should be added.

e. *Galilean invariance*

The inner angular momentum equation (196) is Galilei invariant, as may be shown if one rewrites this equation with the help of the law of mass conservation (59) and the relation (189) as:

$$\varrho\frac{d(vS)}{dt} = -\nabla\cdot J_s - P_A + P'\wedge E' + M'\wedge B',$$
(208)

where $v = \varrho^{-1}$ is the specific volume, d/dt is the material time derivative (159) and the primes denote rest frame quantities (188). From inspection of the various terms of (208) it may be proved that they are all separately Galilei invariant.

7 *The laws of thermodynamics*

a. *The first law*

The first law of thermodynamics for fluid systems with neutral atoms (and for amorphous or polycrystalline solids) will follow from the energy equation (113–114) which may be written as

$$\varrho\frac{d}{dt}(\tfrac{1}{2}v^2+u) = -\nabla\cdot(P\cdot v+J_q)+\varrho\frac{d(vP)}{dt}\cdot E - M\cdot\frac{dB}{dt}$$
$$+v\cdot\{(\nabla E)\cdot P+(\nabla B)\cdot M\},$$
(209)

where (59) and (159) have been used and where $v = \varrho^{-1}$ is the specific volume. At the left-hand side the sum of the specific macroscopic kinetic and internal energies appears. A balance of internal energy alone is obtained if the momentum law (105–106) with (59) or (158) is used in (209):

$$\varrho\frac{du}{dt} = -\nabla\cdot J_q-\tilde{P} : (\nabla v)+\varrho\frac{d(vP)}{dt}\cdot(E+c^{-1}v\wedge B)-(M+c^{-1}v\wedge P)\cdot\frac{dB}{dt},$$
(210)

where $\tilde{P}$ is the transposed pressure tensor. Each of the terms of this balance equation is separately Galilei invariant (v. subsection 5*i*). In particular the rest frame fields and polarizations (188) (up to order c^{-1}) appear (v. (26–27)), so that we may write (210) as

$$\varrho\frac{du}{dt} = -\nabla\cdot J_q-\tilde{P} : \nabla v+\varrho\frac{d(vP')}{dt}\cdot E'-M'\cdot\frac{dB'}{dt}$$
(211)

(it should be remembered that M' is of order c^{-1}). Traditionally one writes the divergence of the heat flow J_q in terms of the 'supplied heat' dq/dt per unit mass and time:

$$\mathbf{\nabla \cdot} J_q = -\varrho \frac{dq}{dt} .$$ (212)

Then (211) gets the form

$$\frac{dq}{dt} = \frac{du}{dt} + v\tilde{\mathbf{P}} : \mathbf{\nabla}v - \frac{d(v\mathbf{P}')}{dt} \cdot E' + vM' \cdot \frac{dB'}{dt} .$$ (213)

This is the *first law of thermodynamics* for fluids (and amorphous or polycrystalline solids) of neutral atoms in an electromagnetic field. If the pressure tensor is a scalar p (times the unit tensor) the second term at the right-hand side reads $vp\mathbf{\nabla \cdot}v$ or, if one uses (59), pdv/dt, the usual form. All quantities of (213) are well-defined as statistical expressions in terms of atomic quantities (v. section 5f). In particular the specific internal energy u has been given by (115) as the sum of the three contributions u^K (78), u^S (97) and u^C (111). It should be noted that the polarization terms in (213) show a special asymmetry, which is a direct consequence of the asymmetry present already on the atomic level (chapter I, section 5b). This asymmetry may of course be removed by means of a Legendre transformation of the internal energy[1]. For instance, with the transformation

$$\hat{u} = u + vM' \cdot B',$$ (214)

one gets instead of (213)

$$\frac{dq}{dt} = \frac{d\hat{u}}{dt} + v\tilde{\mathbf{P}} : \mathbf{\nabla}v - \frac{d(v\mathbf{P}')}{dt} \cdot E' - \frac{d(vM')}{dt} \cdot B'.$$ (215)

However the introduction of the energy $\hat{u}$ is rather artificial: the energy u, in contrast to $\hat{u}$, has a clear-cut physical meaning from the microscopic point of view.

For a neutral plasma the first law of thermodynamics follows from the energy equation (140) with (59), (128), (159), (188) and (212) as

$$\frac{dq}{dt} = \frac{du}{dt} + v\tilde{\mathbf{P}} : \mathbf{\nabla}v - vJ \cdot E',$$ (216)

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[1] For a discussion of various types of Legendre transformations in the first and second laws for magnetized media see for instance H. A. Leupold, Am. J. Phys. **37**(1969)1047. Compare also the microscopic considerations of A. N. Kaufman and T. Soda, J. Chem. Phys. **37**(1962)1988.

where J is the electric current density (purely conductive; the convective part $\varrho^e v$ is not present in a neutral plasma). The 'supplied heat' which figures in the left-hand side and has been given by (212) is essentially the divergence of the heat flow and represents therefore the heat supplied through conduction by the surroundings. The last term at the right-hand side represents the Joule heat produced per unit mass and time.

Finally for systems with correlations of arbitrary range the first law follows from (152) with (59), (150), (159), (188) and (212):

$$\frac{dq}{dt} = \frac{du}{dt} + v\tilde{\mathbf{P}} : \mathbf{\nabla}v - vJ' \cdot E' - \frac{d(v\mathbf{P}')}{dt} \cdot E' + vM' \cdot \frac{dB'}{dt},$$ (217)

where $J' = J - \varrho^e v$ is the rest frame (or conduction) electric current density.

b. *The second law for fluids*

The microscopic basis of the second law of thermodynamics has a character which is different from that of the laws established so far. The latter were all statistical averages of corresponding microscopic equations, whereas the second law contains a new quantity, the entropy, which is not the average of a microscopic quantity. Furthermore the system for which one wants to derive the second law has to be specified in more details as to its statistical properties: here we shall confine ourselves to systems in equilibrium described by a canonical ensemble.

In the present subsection we shall be concerned with the derivation of a second law for systems of neutral atoms in which only short range correlations are present, namely fluids and amorphous or polycrystalline solids.

The theory may be developed along two slightly different lines. In the first conception one considers a system at rest enclosed in a vessel and surrounded by a heat bath in a uniform and time-independent field. As a consequence of the fact that the polarizations are discontinuous at the surface it turns out then that the pressure and related thermodynamic quantities vary over the sample. In the other conception one avoids non-uniformities due to surface effects by dividing a large polarized system into nearly uniform cells, still containing many atoms. These cells are then described by a canonical (or grand) ensemble with their environments playing the role of a heat bath. As external fields the averages of the fields arising from the surroundings of the cell are employed, so that correlations between particles inside and outside the cell are neglected. This is the reason why such an approach is only applicable to systems with short range correlations. We shall

employ it (in this subsection) for fluids and amorphous or polycrystalline solids.

The uniform Maxwell fields E and B in the cell are related to the fields $E_e(R)$ and $B_e(R)$, due to the surroundings of the cell, as

$$E = E_e(R) + P \cdot \int^V \nabla\nabla \frac{1}{4\pi|R - R'|} \, dR',$$

$$B = B_e(R) + M + M \cdot \int^V \nabla\nabla \frac{1}{4\pi|R - R'|} \, dR' \tag{218}$$

(cf. (17)), where P and M are the uniform polarizations in the cell and where the integrals are extended over its volume V. They are to be understood as the sum of a principal value and an integral over a small surface around R (v. problem 1). The equations (218) are satisfied by uniform external fields E_e and B_e if the integral

$$\int^V \nabla\nabla \frac{1}{4\pi|R - R'|} \, dR' \quad (\equiv -\mathbf{L}) \tag{219}$$

is independent of the position R. This is the case if the sample has ellipsoidal shape (see appendix I). In that case the expressions (218) may be written as

$$E = E_e - \mathbf{L} \cdot P,$$

$$B = B_e + M - \mathbf{L} \cdot M, \tag{220}$$

where the tensor $\mathbf{L}$, which is equal to (minus) the integral (219), is called the 'depolarizing tensor'. (It depends on the shape of the boundary.)

The cell will be described with the help of the canonical ensemble

$$e^{-F^*/kT} = C \int e^{-H/kT} \, dq \, dp, \tag{221}$$

where F^* is the free energy[1], T the temperature and C a constant (depending on the number of atoms in the system), while $H(q, p)$ is the Hamiltonian for a dipole system (appendix II, formula (A32), with the atomic charges $e_k = 0$):

---

[1] An asterisk is written at the symbol for the free energy to distinguish it from $F = U - TS$ with U the total internal energy. In fact we shall find that the latter will differ from the average Hamiltonian $\langle H \rangle$, which will be denoted by U^* $(= F^* + TS;$ v. (227) and (232)).

$$H(q, p) = \sum_k \left(\frac{P_k^2}{2m_k} + \sum_{i=1}^{f-1} \frac{p_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{p_{ki} \cdot p_{kj}}{2m_k} \right)$$

$$+ \sum_k \sum_{i,j=1(i \neq j)}^{f} \frac{e_{ki} e_{kj}}{8\pi|R_{ki}(q) - R_{kj}(q)|} + \sum_{k,l(k \neq l)} \sum_{i,j=1}^{f} \frac{e_{ki} e_{lj}}{8\pi|R_{ki}(q) - R_{lj}(q)|}$$

$$- \sum_k \left\{ \bar{\mu}_k^{(1)} \cdot E_e + \left(\bar{v}_k^{(1)} + c^{-1} \bar{\mu}_k^{(1)} \wedge \frac{P_k}{m_k} \right) \cdot B_e \right\}, \tag{222}$$

where $\bar{\mu}_k^{(1)}$ and $\bar{v}_k^{(1)}$ are the electric and magnetic dipole moments.

The free energy F^* is a function of the external fields E_e and B_e, the temperature T and the position of the boundaries of the system. The partial derivatives of the free energy with respect to the external fields follow from (221) and (222):

$$\frac{\partial F^*}{\partial E_e} = -\left\langle \sum_k \bar{\mu}_k^{(1)} \right\rangle = -VP,$$

$$\frac{\partial F^*}{\partial B_e} = -\left\langle \sum_k \left(\bar{v}_k^{(1)} + c^{-1} \bar{\mu}_k^{(1)} \wedge \frac{P_k}{m_k} \right) \right\rangle = -VM, \tag{223}$$

where (65) has been used. The brackets indicate canonical ensemble averages so that for a dynamical variable $a = a(q, p)$ one has the average value $\langle a \rangle = C \int a \exp \{(F^* - H)/kT\} dq \, dp$. Furthermore the partial derivative with respect to the temperature gives the entropy S of the system:

$$\frac{\partial F^*}{\partial T} = -S. \tag{224}$$

The free energy changes also if the boundary changes. We consider infinitesimal variations of the position vector R (choosing the centre of the cell as the origin of the coordinate system):

$$\delta R = \delta\epsilon \cdot R, \tag{225}$$

with a uniform (infinitesimal) deformation tensor $\delta\epsilon$. Then the ellipsoidal shape of the boundaries remains ellipsoidal. (The external fields E_e and B_e may be kept constant during such a deformation by adjusting the charges on condenser plates and currents in coils around the total system in the proper way.)

The total change of the free energy now follows from (223–225):

$$\delta F^* = -S\delta T - VP \cdot \delta E_e - VM \cdot \delta B_e + \mathbf{A} : \delta\epsilon, \tag{226}$$

where the tensor $\mathbf{A}$, which is contracted twice with $\delta\boldsymbol{\epsilon}$ (i.e. $\mathbf{A} : \delta\boldsymbol{\epsilon} \equiv \sum_{i,j} A_{ij}\delta\varepsilon_{ji}$), has still to be determined.

The free energy is connected to the average $\langle H \rangle = U^*$ of the Hamiltonian H by

$$F^* = U^* - TS, \tag{227}$$

where H is given by (222) or by (A37) (with $e_k = 0$). The third term at the right-hand side of (A37) may be expanded as a series if the atoms are outside each other. For that reason we write (A37) in the form

$$H = K + \sum_k \sum_{i,j=1(i\neq j)}^{f} \frac{e_{ki}e_{kj}}{8\pi|\mathbf{R}_{ki}-\mathbf{R}_{kj}|}$$

$$+ \sum_{k,l(k\neq l)} \sum_{n,m=1}^{\infty} \overline{\boldsymbol{\mu}}_k^{(n)} : \mathbf{V}_k^n \overline{\boldsymbol{\mu}}_l^{(m)} : \mathbf{V}_l^m \frac{1}{8\pi|\mathbf{R}_k-\mathbf{R}_l|}$$

$$+ \sum_{k,l(k\neq l)} \left(\sum_{i,j=1}^{f} \frac{e_{ki}e_{lj}}{8\pi|\mathbf{R}_{ki}-\mathbf{R}_{lj}|} - \sum_{n,m=1}^{\infty} \overline{\boldsymbol{\mu}}_k^{(n)} : \mathbf{V}_k^n \overline{\boldsymbol{\mu}}_l^{(m)} : \mathbf{V}_l^m \frac{1}{8\pi|\mathbf{R}_k-\mathbf{R}_l|} \right)$$

$$- \sum_k \overline{\boldsymbol{\mu}}_k^{(1)} \cdot \boldsymbol{E}_e, \tag{228}$$

with K the kinetic energy and where the penultimate term vanishes if the atoms are outside each other. The canonical average of (228) is the total energy of the system. Using (I.41), (I.44), (61) with $v = 0$ and appropriate (time-independent) one- and two-point distribution functions it gets the form

$$U^* \equiv \langle H \rangle = \int \left(\tfrac{1}{2}m\hat{v}_1^2 + \tfrac{1}{2}\sum_i m_i \dot{r}_{1i}^2 + \sum_{i,j(i\neq j)} \frac{e_i e_j}{8\pi|\boldsymbol{r}_{1i}-\boldsymbol{r}_{2j}|} \right) f_1(\boldsymbol{R}_1, 1) \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}1$$

$$+ \int \sum_{n,m=1}^{\infty} \overline{\boldsymbol{\mu}}_1^{(n)} : \mathbf{V}_1^n \overline{\boldsymbol{\mu}}_2^{(m)} : \mathbf{V}_2^m \frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|} f_2(\boldsymbol{R}_1, 1, \boldsymbol{R}_2, 2)\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2\,\mathrm{d}1\,\mathrm{d}2$$

$$+ \int \left(\sum_{i,j} \frac{e_i e_j}{8\pi|\boldsymbol{R}_{1i}-\boldsymbol{R}_{2j}|} - \sum_{n,m=1}^{\infty} \overline{\boldsymbol{\mu}}_1^{(n)} : \mathbf{V}_1^n \overline{\boldsymbol{\mu}}_2^{(m)} : \mathbf{V}_2^m \frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|} \right)$$

$$f_2(\boldsymbol{R}_1, 1, \boldsymbol{R}_2, 2)\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2\,\mathrm{d}1\,\mathrm{d}2$$

$$- \int \overline{\boldsymbol{\mu}}_1^{(1)} \cdot \boldsymbol{E}_e f_1(\boldsymbol{R}_1, \overline{\boldsymbol{\mu}}_1^{(1)})\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\overline{\boldsymbol{\mu}}_1^{(1)}, \tag{229}$$

where the integrals are extended over the volume of the system. Since the system is uniform the integrals over $\boldsymbol{R}_1$ in the first and last terms may be

performed. In the second term we split f_2 into a correlation function of the type (7) and a product of two one-point distribution functions. The latter give rise to an uncorrelated part, in which we omit all multipole moments of orders two and higher (as in subsections 5c, d such moments would yield terms containing macroscopic multipole densities of higher order, which are assumed to be negligible in our system). We then obtain

$$U^* = V\varrho u^{\mathrm{K}} + PP : \int \mathbf{V}_1 \mathbf{V}_2 \frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|} \mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2$$

$$+ \int \sum_{n,m=1}^{\infty} (-1)^m \overline{\boldsymbol{\mu}}_1^{(n)} : \mathbf{V}_s^n \overline{\boldsymbol{\mu}}_2^{(m)} : \mathbf{V}_s^m \frac{1}{8\pi s} c_2(\boldsymbol{R}+\tfrac{1}{2}s, 1, \boldsymbol{R}-\tfrac{1}{2}s, 2)\mathrm{d}\boldsymbol{R}\,\mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2$$

$$+ \int \left(\sum_{i,j} \frac{e_i e_j}{8\pi|s+\boldsymbol{r}_{1i}-\boldsymbol{r}_{2j}|} - \sum_{n,m=1}^{\infty} (-1)^m \overline{\boldsymbol{\mu}}_1^{(n)} : \mathbf{V}_s^n \overline{\boldsymbol{\mu}}_2^{(m)} : \mathbf{V}_s^m \frac{1}{8\pi s} \right)$$

$$f_2(\boldsymbol{R}+\tfrac{1}{2}s, 1, \boldsymbol{R}-\tfrac{1}{2}s, 2)\mathrm{d}\boldsymbol{R}\,\mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2 - \boldsymbol{P}\cdot\boldsymbol{E}_e, \tag{230}$$

where (65) and (78) have been used, and new integration variables $\boldsymbol{R}$ and s have been introduced in the third and fourth terms at the right-hand side. The limits of the integration over s depend on the value of the variable $\boldsymbol{R}$. However since both the correlation length and the dimension of the atoms (which is the range of the first factor in the integrand of the fourth term) are small compared to the dimension of the system, effectively the limits of the integration over s depend on $\boldsymbol{R}$ only in a small region near the surface. Neglecting these surface effects, and using the fact that the system is uniform, we perform the integrals over $\boldsymbol{R}$ in the third and fourth term. Furthermore the integral in the second term may be written as (see appendix I):

$$\int \mathbf{V}_1 \mathbf{V}_2 \frac{1}{4\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|} \mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2 = -V \int^{V} \mathbf{V}\mathbf{V} \frac{1}{4\pi|\boldsymbol{R}|} \mathrm{d}\boldsymbol{R} \equiv V\mathbf{L}, \tag{231}$$

where $\boldsymbol{R}$ is the position with respect to the centre of the ellipsoid and where $\mathbf{L}$ is the depolarizing tensor (which depends on the shape of the system). In this way we obtain as the average Hamiltonian, using the internal energy u (115) with (97) (neutral atoms have $\overline{\mu}_k^{(0)} = 0$) and (111)

$$U^* = U + V(\tfrac{1}{2}PP : \mathbf{L} - \boldsymbol{P}\cdot\boldsymbol{E}_e), \tag{232}$$

with $U = V\varrho u$ the total internal energy.

Finally the tensor $\mathbf{A}$ occurring in (226) has to be found. In appendix III it is proved that $\mathbf{A}$ is the following average

$$\mathbf{A} = - \left\langle \sum_k \left(\frac{\partial H}{\partial \boldsymbol{P}_k} \boldsymbol{P}_k - \boldsymbol{R}_k \frac{\partial H}{\partial \boldsymbol{R}_k} \right) \right\rangle \tag{233}$$

with R_k and P_k the canonical centre of mass coordinates and momenta of atom k. We substitute into this expression the Hamiltonian (222), add and subtract the multipole series expansion of the third term and use the appropriate time-independent distribution functions. This gives

$$A = -\int m\hat{v}_1 \, \hat{v}_1 \, f_1(R_1, v_1)\mathrm{d}R_1 \, \mathrm{d}v_1$$

$$+ \int \sum_{n,m=1}^{\infty} \left\{ (R_1 - R_2)\nabla_1 \, \overline{\mu}_1^{(n)} : \nabla_1^n \overline{\mu}_2^{(m)} : \nabla_2^m \frac{1}{8\pi|R_1 - R_2|} \right\}$$

$$f_2(R_1, 1, R_2, 2)\mathrm{d}R_1 \, \mathrm{d}R_2 \, \mathrm{d}1 \, \mathrm{d}2$$

$$+ \int \left\{ (R_1 - R_2)\nabla_1 \left(\sum_{i,j} \frac{e_i e_j}{8\pi|R_{1i} - R_{2j}|} \right. \right.$$

$$\left. \left. - \sum_{n,m=1}^{\infty} \overline{\mu}_1^{(n)} : \nabla_1^n \overline{\mu}_2^{(m)} : \nabla_2^m \frac{1}{8\pi|R_1 - R_2|} \right) \right\} f_2(R_1, 1, R_2, 2)\mathrm{d}R_1 \, \mathrm{d}R_2 \, \mathrm{d}1 \, \mathrm{d}2$$

$$+ c^{-1} \int \hat{v}_1 \, \overline{\mu}_1^{(1)} \wedge B_e \, f_1(R_1, v_1, \overline{\mu}_1^{(1)})\mathrm{d}R_1 \, \mathrm{d}v_1 \, \mathrm{d}\overline{\mu}_1^{(1)}, \tag{234}$$

where we used the Hamilton equation $v_k \equiv \dot{R}_k = \partial H/\partial P_k$ and the expression (61) with $v = 0$. Because of the uniformity of the system the space integrals in the first and last terms may be performed. Then they become, apart from a factor $-V$, equal to the sum of the kinetic pressure P^K (63) and the field dependent part of the pressure P^F (73). In the second term we introduce a correlation function with the help of (7). In the uncorrelated part we omit all multipole moments of order 2 and higher, as in (230). In this way we obtain for (234)

$$A = -V(P^K + P^F) + \int (R_1 - R_2)\nabla_1 \, P\cdot\nabla_1 \, P\cdot\nabla_2 \frac{1}{8\pi|R_1 - R_2|} \, \mathrm{d}R_1 \, \mathrm{d}R_2$$

$$+ \int \sum_{n,m=1}^{\infty} (-1)^m \left(s\nabla_s \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right)$$

$$c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2)\mathrm{d}R \, \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2$$

$$+ \int \left\{ s\nabla_s \left(\sum_{i,j} \frac{e_i e_j}{8\pi|s + r_{1i} - r_{2j}|} - \sum_{n,m=1}^{\infty} (-1)^m \overline{\mu}_1^{(n)} : \nabla_s^n \overline{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right) \right\}$$

$$f_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2)\mathrm{d}R \, \mathrm{d}s \, \mathrm{d}1 \, \mathrm{d}2, \tag{235}$$

where (65) has been used and new integration variables R and s have been introduced. Just as for the Hamiltonian, the integrations over s in the third and fourth term are effectively to be extended over a volume small compared

to that of the system, so that the integration over R may be performed, the system being uniform. Furthermore the second term may be written as (see appendix I):

$$\int (R_1 - R_2)\nabla_1 \, \nabla_1 \, \nabla_2 \frac{1}{8\pi|R_1 - R_2|} \, \mathrm{d}R_1 \, \mathrm{d}R_2$$

$$= -V \int R\nabla\nabla\nabla \frac{1}{8\pi|R|} \, \mathrm{d}R \equiv -\tfrac{1}{2}V\mathbf{K}, \tag{236}$$

where R measures the position relative to the centre of the system and $\mathbf{K}$ is a tensor of the fourth rank, which depends on the shape of the boundary of the ellipsoidal system. In this way we obtain for (235), using (107) with (94) and (104),

$$A = -V(P + \tfrac{1}{2}\mathbf{K} : PP), \tag{237}$$

where P is the pressure tensor and the last indices of $\mathbf{K}$ are contracted with those of the two factors P (the electric polarization).

This result could have been found along different lines, namely by starting from the expression (A48) of appendix III according to which

$$\delta_\varepsilon F^* = -\int^S n\cdot P_{\text{out}}\cdot\delta\boldsymbol{\varepsilon}\cdot R \, \mathrm{d}S, \tag{238}$$

where P_{out} is the pressure exerted by a wall (supposed to be unpolarizable) which separates the cell from its surroundings and n is the normal to the wall. This pressure is not equal to the pressure P, just inside the boundary. The reason for this difference is that the electromagnetic fields are discontinuous across the boundary. In fact it follows from momentum conservation in the form (109), applied to a thin volume element with surfaces on either side of the boundary between the separation wall and the cell, that for a system in equilibrium and at rest one has

$$n\cdot(P - P_{\text{out}}) = n\cdot\{DE + BH - (\tfrac{1}{2}E^2 + \tfrac{1}{2}B^2 - M\cdot B)U\}$$

$$- n\cdot\{EE + BB - (\tfrac{1}{2}E^2 + \tfrac{1}{2}B^2)U\}_{\text{out}}. \tag{239}$$

The fields just inside the cell and inside the separation wall are connected by relations which are consequences of the Maxwell equations:

$$n\cdot D = n\cdot E_{\text{out}}, \qquad E - nn\cdot E = E_{\text{out}} - nn\cdot E_{\text{out}},$$

$$n\cdot B = n\cdot B_{\text{out}}, \qquad H - nn\cdot H = B_{\text{out}} - nn\cdot B_{\text{out}}. \tag{240}$$

Insertion of these formulae into (239) leads to

$$n\cdot(P - P_{\text{out}}) = -\tfrac{1}{2}n(P\cdot n)^2, \tag{241}$$

up to order c^{-1}. (Terms quadratic in the magnetization are of order c^{-2} and hence not considered in the non-relativistic theory.) The right-hand side of equation (241) is usually called the Liénard pressure[1]. (Incidentally this formula shows how one could measure the pressure $\mathbf{P}$ just inside a polarizable system: $\mathbf{P}_{out}$ may be measured by means of a manometer made of unpolarizable material, while a value of the polarization P may be obtained independently.) If one introduces (241) into (238) and uses the assumed uniformity of $\mathbf{P}$ and $\delta\boldsymbol{\epsilon}$ one finds

$$\delta_\varepsilon F^* = -V\mathbf{P} : \delta\boldsymbol{\epsilon} - \tfrac{1}{2}\int^S \boldsymbol{n}\cdot\delta\boldsymbol{\epsilon}\cdot\boldsymbol{R}(\boldsymbol{P}\cdot\boldsymbol{n})^2\,\mathrm{d}S. \qquad (242)$$

This expression is indeed equal to $\mathbf{A} : \delta\boldsymbol{\epsilon}$ with $\mathbf{A}$ given by (237) as follows with the help of the identity valid for the tensor $\mathbf{K}$ (defined in (236)) of a volume of ellipsoidal shape (v. problem 5)

$$\mathbf{K} = \frac{1}{V}\int^S \boldsymbol{R}\boldsymbol{n}\boldsymbol{n}\boldsymbol{n}\,\mathrm{d}S. \qquad (243)$$

Collecting the results (223), (224) and (237) and substituting them into (226) with (227), we have found now for the change of the entropy

$$T\delta S = \delta U^* + V(\mathbf{P} + \tfrac{1}{2}\mathbf{K} : \boldsymbol{P}\boldsymbol{P}) : \delta\boldsymbol{\epsilon} + V\boldsymbol{P}\cdot\delta\boldsymbol{E}_\mathrm{e} + V\boldsymbol{M}\cdot\delta\boldsymbol{B}_\mathrm{e}. \qquad (244)$$

If one inserts moreover (232) one obtains, dividing the result by the total (constant) mass M of the system:

$$T\delta s = \delta(u + \tfrac{1}{2}v\boldsymbol{P}\boldsymbol{P} : \mathbf{L}) + v(\mathbf{P} + \tfrac{1}{2}\mathbf{K} : \boldsymbol{P}\boldsymbol{P}) : \delta\boldsymbol{\epsilon} - \boldsymbol{E}_\mathrm{e}\cdot\delta(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\delta\boldsymbol{B}_\mathrm{e}, \qquad (245)$$

where $s = S/M$ is the specific entropy and $v = V/M$ the specific volume. In this relation the external fields occur, *not* the Maxwell fields. We may introduce the latter instead of the former, by using (220) and also the relation (proved in appendix I) that gives the change of the depolarizing tensor if the shape of the boundary is changed:

$$\delta(v^{-1}\mathbf{L}) = -v^{-1}\delta\boldsymbol{\epsilon} : \mathbf{K}. \qquad (246)$$

We then obtain, up to order c^{-1} (noting that $\boldsymbol{M}$ is of order c^{-1} already) the entropy law

$$T\delta s = \delta u + v\mathbf{P} : \delta\boldsymbol{\epsilon} - \boldsymbol{E}\cdot\delta(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\delta\boldsymbol{B}. \qquad (247)$$

This law will be further studied, first for fluids, then for amorphous or polycrystalline substances.

[1] A. Liénard, Ann. Physique **20**(1923)249.

A *fluid* system at rest is isotropic in the absence of polarizations and fields. Then the entropy depends only on the internal energy u and the specific volume v, not on the shape of the boundary. Therefore in this case only the scalar part of the tensor $\delta\boldsymbol{\epsilon}$ should contribute to the second term and hence $\mathbf{P}$ reduces to a scalar p (times the unit tensor $\mathbf{U}$). In this way, since $v\mathbf{U} : \delta\boldsymbol{\epsilon}$ is the change of volume δv, the entropy law (247) becomes then

$$T\mathrm{d}s = \mathrm{d}u + p\,\mathrm{d}v, \qquad (248)$$

where we have written differentials, because now s is a function of u and v.

If fields and polarizations are present, it is not immediately clear that again $\mathbf{P}$ is diagonal, since now the isotropy of the system is perturbed. However, if the polarization vectors P, M are assumed to depend only on the specific volume v, the specific entropy s (or temperature) and the fields, i.e.

$$P = P(v, s, E, B), \qquad M = M(v, s, E, B), \qquad (249)$$

the entropy law (247) may be integrated at constant $\boldsymbol{\epsilon}$ and s with the result

$$u = u_0 + \Delta u, \qquad (250)$$

where u_0 is the specific energy at zero polarizations and fields, which depends only on v and s. Furthermore Δu is a function of v, s, E and B or (with (249)) of v, s, vP and B. Therefore u depends on these variables so that δu contains only the trace of $\delta\boldsymbol{\epsilon}$ which is equal to $v^{-1}\delta v$. Hence from (247) it follows that in equilibrium the tensor $\mathbf{P}$ reduces to a scalar pressure $p\mathbf{U}$ for the fluid systems studied. So finally the non-relativistic second law (or 'Gibbs relation') becomes for a (one-component) fluid of neutral atoms

$$T\mathrm{d}s = \mathrm{d}u + p\,\mathrm{d}v - \boldsymbol{E}\cdot\mathrm{d}(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\mathrm{d}\boldsymbol{B}. \qquad (251)$$

(It should be kept in mind that all quantities have been defined for a system at rest. In particular the fields and polarizations are therefore the same as the primed quantities of the preceding subsection.) The field terms in the second law (251) show the same asymmetry as has been discussed in connexion with those appearing in the first law (213).

For *amorphous* or *polycrystalline* substances it is not possible to reduce the entropy law (247) to the simple form (251): the pressure tensor does not reduce to a multiple of the unit tensor. In order to obtain a Gibbs relation from (247) we start by expressing the infinitesimal deformation $\delta\boldsymbol{\epsilon}$ in terms of state variables; $\delta\boldsymbol{\epsilon}$ itself is not a stable variable as its definition (225) shows, because R is the position of a point in the deformed state. Let us introduce, as state variables characterizing the position R of a point of the substance in terms of its position R° in a fixed reference state (denoted by

the symbol $^{\circ}$), a tensor $\hat{\boldsymbol{\eta}}$ by means of the relation

$$\boldsymbol{R} = \hat{\boldsymbol{\eta}}\cdot\boldsymbol{R}^{\circ}. \tag{252}$$

Here $\hat{\boldsymbol{\eta}}$ is independent of $\boldsymbol{R}$ since only uniform deformations of the (uniform) cell are considered. Comparison of (252) with (225) shows that one has for $\delta\boldsymbol{\epsilon}$:

$$\delta\boldsymbol{\epsilon} = \delta\hat{\boldsymbol{\eta}}\cdot\hat{\boldsymbol{\eta}}^{-1}. \tag{253}$$

In this way $\delta\boldsymbol{\epsilon}$ is expressed in variations of the state variable $\hat{\boldsymbol{\eta}}$.

It is convenient to write the deformation tensor $\hat{\boldsymbol{\eta}}$ as a product of a symmetric 'dilatation' tensor $\boldsymbol{\eta}$ ($= \tilde{\boldsymbol{\eta}}$, the transposed tensor). and an orthogonal 'rotation' tensor $\boldsymbol{\eta}_A$ (so that $\tilde{\boldsymbol{\eta}}_A = \boldsymbol{\eta}_A^{-1}$):

$$\hat{\boldsymbol{\eta}} = \boldsymbol{\eta}_A\cdot\boldsymbol{\eta}. \tag{254}$$

If the sample is only slightly deformable the tensor $\boldsymbol{\eta}$ is nearly equal to the unit tensor $\mathbf{U}$. Furthermore the tensor $\boldsymbol{\eta}_A$ might be parametrized in terms of three angles, for instance the Eulerian angles. Introducing (254) into (253) we get for the variation

$$\delta\boldsymbol{\epsilon} = (\delta\boldsymbol{\eta}_A\cdot\boldsymbol{\eta} + \boldsymbol{\eta}_A\cdot\delta\boldsymbol{\eta})\cdot\boldsymbol{\eta}^{-1}\cdot\boldsymbol{\eta}_A^{-1} \simeq \delta\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A + \boldsymbol{\eta}_A\cdot\delta\boldsymbol{\eta}\cdot\tilde{\boldsymbol{\eta}}_A, \tag{255}$$

where in the second expression $\boldsymbol{\eta}$ could be replaced by the unit tensor. The first term in the last member of (255) is antisymmetric as follows from $\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A = \mathbf{U}$, while the second term is symmetric, since $\delta\boldsymbol{\eta}$ is symmetric and $\boldsymbol{\eta}_A$ orthogonal. With the help of (255) we obtain as the second law for an amorphous or polycrystalline solid:

$$T\mathrm{d}s = \mathrm{d}u + v(\boldsymbol{\eta}_A\cdot\mathbf{P}\cdot\boldsymbol{\eta}_A) : \mathrm{d}\boldsymbol{\eta} + v\mathbf{P} : (\mathrm{d}\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A) - \boldsymbol{E}\cdot\mathrm{d}(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\mathrm{d}\boldsymbol{B}, \tag{256}$$

which is written with differentials since now all quantities are state variables. In the second term at the right-hand side only the symmetrical part $\mathbf{P}_S = \frac{1}{2}(\mathbf{P}+\tilde{\mathbf{P}})$ of the pressure contributes, since $\mathrm{d}\boldsymbol{\eta}$ is symmetric and $\boldsymbol{\eta}_A$ is orthogonal. In the third term only the antisymmetrical part $\frac{1}{2}(\mathbf{P}-\tilde{\mathbf{P}})$ remains, because the bracket expression is antisymmetric. From the angular momentum balance equation (196) it follows by employing the uniformity of the cell that

$$\mathbf{P}_A = \boldsymbol{P}\wedge\boldsymbol{E} + \boldsymbol{M}\wedge\boldsymbol{B}, \tag{257}$$

or alternatively,

$$\tfrac{1}{2}(\mathbf{P}-\tilde{\mathbf{P}}) = \tfrac{1}{2}(\boldsymbol{P}\boldsymbol{E} - \boldsymbol{E}\boldsymbol{P} + \boldsymbol{M}\boldsymbol{B} - \boldsymbol{B}\boldsymbol{M}). \tag{258}$$

Then the second law (256) becomes

$$T\mathrm{d}s = \mathrm{d}u + v(\boldsymbol{\eta}_A\cdot\mathbf{P}_S\cdot\boldsymbol{\eta}_A) : \mathrm{d}\boldsymbol{\eta} + v(\boldsymbol{P}\boldsymbol{E} + \boldsymbol{M}\boldsymbol{B}) : (\mathrm{d}\boldsymbol{\eta}_A\cdot\boldsymbol{\eta}_A) - \boldsymbol{E}\cdot\mathrm{d}(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\mathrm{d}\boldsymbol{B}. \tag{259}$$

This form shows that the entropy changes not only through a change of the internal energy and through symmetric deformations, but also due to effects of the electromagnetic fields as is apparent from the last three terms. The first of the latter in particular shows the effect of rotation of the ellipsoidal cell as a whole in the external field. (If desired so, the tensor $\boldsymbol{\eta}_A$ may be expressed in terms of the three Euler angles with respect to a fixed reference state.)

Often the polarizations are parallel to the fields for amorphous and polycrystalline solids. Then (257), (258) and the third term at the right-hand side of (259) vanish, so that we are left with the second law

$$T\mathrm{d}s = \mathrm{d}u + v(\tilde{\boldsymbol{\eta}}_A\cdot\mathbf{P}_S\cdot\boldsymbol{\eta}_A) : \mathrm{d}\boldsymbol{\eta} - \boldsymbol{E}\cdot\mathrm{d}(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\mathrm{d}\boldsymbol{B}. \tag{260}$$

In this way the Gibbs relations for uniform fluids and amorphous or polycrystalline solids have been found as the laws (251) and (260). The only difference between these two cases consists in the occurrence of a pressure tensor in (260) and a scalar pressure in (251).

c. *The second law for plasmas*

The method used to derive a second law for fluids will be employed in this subsection to find that for plasmas.

Let us consider a uniform cell as a subsystem of a neutral plasma at rest in a uniform and constant field. The plasma is a mixture of charged particles of which the internal structure is disregarded. In such a system the uniform Maxwell fields are connected to the fields $\boldsymbol{E}_c(\boldsymbol{R})$ and $\boldsymbol{B}_c(\boldsymbol{R})$ from outside the cell as (v. (17))

$$\begin{aligned}
\boldsymbol{E} &= \boldsymbol{E}_c(\boldsymbol{R}) - \varrho^e\nabla\int\frac{1}{4\pi|\boldsymbol{R}-\boldsymbol{R}'|}\,\mathrm{d}R', \\
\boldsymbol{B} &= \boldsymbol{B}_c(\boldsymbol{R}) - c^{-1}\boldsymbol{J}\wedge\nabla\int\frac{1}{4\pi|\boldsymbol{R}-\boldsymbol{R}'|}\,\mathrm{d}R',
\end{aligned} \tag{261}$$

where ϱ^e and $\boldsymbol{J}$ are the uniform charge and current densities. Hence the external fields are uniform only if the macroscopic charge and current densities ϱ^e and $\boldsymbol{J}$ vanish. For that reason we only consider neutral plasmas without currents. Then the Maxwell fields are equal to the external fields.

The Hamiltonian for the plasma is (cf. (A26) or (A32) of appendix II)

$$H = \sum_k\frac{\boldsymbol{P}_k^2}{2m_k} + \sum_{k,l(k\neq l)}\frac{e_k e_l}{8\pi|\boldsymbol{R}_k - \boldsymbol{R}_l|} + \sum_k e_k\left\{\varphi_e(\boldsymbol{R}_k) - c^{-1}\frac{\boldsymbol{P}_k}{m_k}\cdot\boldsymbol{A}_e(\boldsymbol{R}_k)\right\}. \tag{262}$$

The potentials describe a constant and uniform external field and may thus be chosen as

$$\varphi_e(R_k) = -R_k \cdot E_e,$$
$$A_e(R_k) = \tfrac{1}{2} B_e \wedge R_k. \tag{263}$$

(If a different gauge would have been used, the resulting Hamiltonian might be transformed to (262) with (263) by means of a canonical transformation.)

The free energy[1] F is again a function of the external fields E_e, B_e, the temperature T and the position of the boundary of the system. The partial derivatives with respect to the external fields and the temperature are up to order c^{-1}:

$$\frac{\partial F}{\partial E_e} = -\int R \varrho^e(R) dR = 0,$$
$$\frac{\partial F}{\partial B_e} = -\tfrac{1}{2} c^{-1} \int R \wedge J(R) dR = 0, \tag{264}$$

with the charge and current densities (124), and

$$\frac{\partial F}{\partial T} = -S. \tag{265}$$

In this way we get for the change of the free energy

$$\delta F = -S \delta T + A : \delta \epsilon, \tag{266}$$

where A has still to be determined.

The free energy $F = \langle H \rangle - TS$ follows from the average of the Hamiltonian (cf. (A37)) for the plasma

$$H = K + \sum_{k,l(k \neq l)} \frac{e_k e_l}{8\pi |R_k - R_l|} + \sum_k e_k \varphi_e(R_k). \tag{267}$$

The average of this expression is

$$\langle H \rangle = \sum_a \int \tfrac{1}{2} m_a \hat{v}_1^2 f_1^a(R_1, v_1) dR_1 dv_1$$
$$+ \sum_{a,b} \int \frac{e_a e_b}{8\pi |R_1 - R_2|} f_2^{ab}(R_1, R_2) dR_1 dR_2, \tag{268}$$

where (263) and the vanishing of the charge density have been taken into account. In the first term the integration over R_1 may be performed as a

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[1] Here the free energy is denoted by a symbol F without asterisk, since it will turn out that the average Hamiltonian $\langle H \rangle$ is equal to the total internal energy (v. (270)).

consequence of the uniformity of the system. In the second term we write f_2^{ab} as the sum of a correlation function c_2^{ab} and the product $f_1^a f_1^b$. The latter, uncorrelated part gives no contribution, since the charge density vanishes, so that we obtain now, using also (131)

$$\langle H \rangle = V \varrho u^K + \sum_{a,b} \int \frac{e_a e_b}{8\pi s} c_2^{ab}(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s) dR ds. \tag{269}$$

For neutral plasmas in equilibrium the correlation function has short range. Then the integral over R may be performed, since the system is uniform. In this way we get with (138) and (141)

$$\langle H \rangle = V \varrho u. \tag{270}$$

The tensor A, which occurs in (266), follows from (A55) of appendix III with (262):

$$A = -\sum_a \int m_a \hat{v}_1 \hat{v}_1 f_1^a(R_1, v_1) dR_1 dv_1 - \sum_a e_a \int R_1 E_e f_1^a(R_1) dR_1$$
$$+ \tfrac{1}{2} c^{-1} \sum_a \int e_a \{\hat{v}_1(R_1 \wedge B_e) - R_1(\hat{v}_1 \wedge B_e)\} f_1^a(R_1, v_1) dR_1 dv_1$$
$$+ \sum_{a,b} \int (R_1 - R_2) \nabla_1 \frac{e_a e_b}{8\pi |R_1 - R_2|} f_2^{ab}(R_1, R_2) dR_1 dR_2, \tag{271}$$

where we have used the Hamilton equation $\partial H / \partial P_k = \dot{R}_k \equiv v_k$. In the first term the integration over R_1 may be performed. In the second and third terms one recognizes the charge and current densities (124), which vanish in the plasma studied. In the fourth term we split f_2^{ab} into c_2^{ab} and $f_1^a f_1^b$. Again the latter part gives no contribution because the charge density is zero. In this way (271) becomes, with the help of (122),

$$A = -V P^K + \sum_{a,b} \int s \nabla_s \frac{e_a e_b}{8\pi s} c_2^{ab}(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s) dR ds. \tag{272}$$

The integration over R may be performed owing to the short range character of the correlation function. Then we get with (127) and (129):

$$A = -V P. \tag{273}$$

So finally we obtain from (266), with (264), (265), (270) and (273), dividing by the total mass M,

$$T \delta s = \delta u + v P : \delta \epsilon, \tag{274}$$

where $s = S/M$ and $v = V/M$ are the specific entropy and volume. From

(274) it follows that the specific energy at constant s and ϵ does not change if fields are switched on:

$$u = u_0, \tag{275}$$

where u_0 is the specific energy at zero fields, which depends only on u and s, since the plasma is isotropic in the absence of fields. So in (274) only the trace of $\delta\epsilon$ (which is equal to $v^{-1}\delta v$) may occur. Therefore the second law for a neutral and current-free plasma becomes

$$T\mathrm{d}s = \mathrm{d}u + p\,\mathrm{d}v, \tag{276}$$

showing that the pressure tensor in a plasma reduces to a scalar at equilibrium.

d. *The second law for crystalline solids*

For the systems with short range correlations treated so far we derived the second law of thermodynamics by considering a uniform cell as a sub-system of a larger system, which played the role of a heat bath. For the case of systems with long range correlations – as crystalline solids – such a division of the system into cells is no longer feasible. One has to consider in that case the system as a whole. As a consequence one can no longer suppose that the system is uniform: non-uniformities will enter the system through boundary effects (even if simple shapes are chosen for this boundary).

We use again the canonical ensemble to describe the system in uniform external fields in a heat bath, limiting ourselves to systems without space charge. Then the existence of a thermodynamic limit has been proved[1]. At equilibrium the electric current density in the system at rest will vanish (since then both the conduction and convection currents are zero). The Hamiltonian is given by (A32) with the potentials (263) for the uniform external fields. The partial derivatives of the free energy with respect to the external fields are, up to order c^{-1},

$$\frac{\partial F^*}{\partial E_\mathrm{e}} = -\Big\langle \sum_k \big(e_k R_k + \bar{\mu}_k^{(1)}\big)\Big\rangle = -\int P(R)\mathrm{d}R,$$

$$\frac{\partial F^*}{\partial B_\mathrm{e}} = -\Big\langle \sum_k \Big(\tfrac{1}{2}c^{-1}e_k R_k \wedge \frac{P_k}{m_k} + \bar{v}_k^{(1)} + c^{-1}\bar{\mu}_k^{(1)} \wedge \frac{P_k}{m_k}\Big)\Big\rangle = -\int M(R)\mathrm{d}R, \tag{277}$$

where the expressions (64–65) have been used and the fact that the charge and current densities vanish. Furthermore the partial derivative of the free

[1] J. L. Lebowitz and E. H. Lieb, Phys. Rev. Lett. **22**(1969)631.

energy with respect to the temperature is

$$\frac{\partial F^*}{\partial T} = -S. \tag{278}$$

The total change of the free energy is now

$$\delta F^* = -S\delta T - V\bar{P}\cdot\delta E_\mathrm{e} - V\bar{M}\cdot\delta B_\mathrm{e} + \delta_\varepsilon F^*, \tag{279}$$

where we have introduced the notation $\bar{X}$ for space averages of a quantity $X(R)$:

$$\bar{X} \equiv \frac{1}{V}\int X(R)\mathrm{d}R, \tag{280}$$

and where $\delta_\varepsilon F^*$ is the change of the free energy through deformations. The canonical average $\langle H \rangle \equiv U^*$ of the Hamiltonian (A37) with (263) is (cf. (232))

$$U^* = U - \int P(R_1)P(R_2) : \nabla_1\nabla_1 \frac{1}{8\pi|R_1 - R_2|}\mathrm{d}R_1\,\mathrm{d}R_2 - V\bar{P}\cdot E_\mathrm{e}, \tag{281}$$

where (115) with (78), (97) and (153) have been used and where U is the total internal energy $V\varrho\bar{u}$ of the system.

The change of the free energy $\delta_\varepsilon F^*$ under deformations follows from (A53) of appendix III, with the Hamiltonian (A32). The term with the deformation gradient tensor δe in (A53) gives

$$-\int \{\mathbf{P}^\mathrm{K}(R) + \mathbf{P}^\mathrm{F}(R)\} : \delta e(R)\mathrm{d}R, \tag{282}$$

as follows from the explicit forms (63) and (73) of the kinetic and 'field' part of the pressure tensor. The term with $\delta\epsilon$ in (A53) becomes upon introduction of (A32)

$$\Big\langle \sum_{k,l(k\neq l)} \sum_{i,j} \{R_k\cdot\delta\tilde{\epsilon}(R_k) - R_l\cdot\delta\tilde{\epsilon}(R_l)\}\cdot\nabla_k \frac{e_{ki}e_{lj}}{8\pi|R_{ki} - R_{lj}|}\Big\rangle. \tag{283}$$

If this expression is split into a long range and a short range part by making a multipole expansion and if appropriate two-point distribution and correlation functions are introduced, one finds

$$-\int \{R_1\cdot\delta\tilde{\epsilon}(R_1) - R_2\cdot\delta\tilde{\epsilon}(R_2)\}P(R_1)P(R_2) : \nabla_1\nabla_1\nabla_1 \frac{1}{8\pi|R_1 - R_2|}\mathrm{d}R_1\,\mathrm{d}R_2$$

$$+ \int \Big[\{(R + \tfrac{1}{2}s)\cdot\delta\tilde{\epsilon}(R + \tfrac{1}{2}s) - (R - \tfrac{1}{2}s)\cdot\delta\tilde{\epsilon}(R - \tfrac{1}{2}s)\}\cdot\nabla_s \sum_{n,m=0}^{\infty} (-1)^m \bar{\mu}_1^{(n)}$$

$$: \nabla_s^n \bar{\mu}_2^{(m)} : \nabla_s^m \frac{1}{8\pi s}\Big] c_2(R + \tfrac{1}{2}s, 1, R - \tfrac{1}{2}s, 2)\mathrm{d}R\,\mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2$$

$$+ \int \left[\{(R+\tfrac{1}{2}s)\cdot\delta\bar{\epsilon}(R+\tfrac{1}{2}s) - (R-\tfrac{1}{2}s)\cdot\delta\bar{\epsilon}(R-\tfrac{1}{2}s)\}\cdot\mathbf{V}_s \left(\sum_{i,j} \frac{e_{1i}e_{2j}}{8\pi|s+r_{1i}-r_{2j}|} \right. \right.$$

$$\left. \left. - \sum_{n,m=0}^{\infty} (-1)^m \bar{\mu}_1^{(n)} \vdots \mathbf{V}_s^n \bar{\mu}_2^{(m)} \vdots \mathbf{V}_s^m \frac{1}{8\pi s} \right) \right]$$

$$f_2(R+\tfrac{1}{2}s, 1, R-\tfrac{1}{2}s, 2)\mathrm{d}R\,\mathrm{d}s\,\mathrm{d}1\,\mathrm{d}2, \quad (284)$$

where in the second and third term we introduced the variables R and s, connected with R_1 and R_2 by $R_1 = R+\tfrac{1}{2}s$ and $R_2 = R-\tfrac{1}{2}s$. In the last term the integration over s is extended over small values of s only, so that one may expand the factors $(R\pm\tfrac{1}{2}s)\cdot\delta\bar{\epsilon}(R\pm\tfrac{1}{2}s)$ around $R\cdot\delta\bar{\epsilon}(R)$ and break off after the second term. Then the last term of (284) becomes

$$-\int \mathbf{P}^{\mathrm{S}}(R) : \delta e(R)\mathrm{d}R, \quad (285)$$

where we introduced the short range pressure tensor (94) and the tensor δe (A51). The second term in (284) may be written in the form

$$-\int \mathbf{P}^{\mathrm{C}}(R) : \delta e(R)\mathrm{d}R, \quad (286)$$

as we shall now prove. To that end we introduce the correlation pressure (151) into (286); owing to the symmetry of the integrand of (151) one may employ $c_2^{\pm}$ (202) instead of c_2^{+} (149). Then one gets

$$-\int \mathbf{P}^{\mathrm{C}}(R) : \delta e(R)\mathrm{d}R = \int_{-1}^{1} \mathrm{d}\lambda \int_{-\infty}^{\infty} \mathrm{d}R' \int_{-\infty}^{\infty} \mathrm{d}s \int \mathrm{d}1\,\mathrm{d}2 \sum_{n,m=0}^{\infty} (-1)^m$$

$$\left\{ s\cdot\delta\bar{\epsilon}(R'-\tfrac{1}{2}\lambda s)\cdot\mathbf{V}_s \bar{\mu}_1^{(n)} \vdots \mathbf{V}_s^n \bar{\mu}_2^{(m)} \vdots \mathbf{V}_s^m \frac{1}{16\pi s} \right\} c_2(R'+\tfrac{1}{2}s, 1, R'-\tfrac{1}{2}s, 2), \quad (287)$$

where we introduced the integration variables $R' = R+\tfrac{1}{2}\lambda s$. Effectively the integrations over R' and s just as those over R and s are extended over those values for which the arguments of the correlation function are inside the volume of the system. Since the correlation function vanishes if these arguments indicate positions outside the volume, we may for convenience write $-\infty$ and ∞ as integration limits. The first factor in the integrand in (287) may be written in an alternative form

$$s\cdot\delta\tilde{\epsilon}(R'-\tfrac{1}{2}\lambda s)\cdot\mathbf{V}_s = -2\frac{\partial}{\partial\lambda}\{(R'-\tfrac{1}{2}\lambda s)\cdot\delta\bar{\epsilon}(R'-\tfrac{1}{2}\lambda s)\}\cdot\mathbf{V}_s, \quad (288)$$

if we use the definition (A51) of δe. If this expression is inserted into (287)

the integration over λ may be performed. Then one recovers indeed the second term of (284).

We have found now for the change of the free energy under deformations

$$\delta_\varepsilon F^* = -\int \mathbf{P}(R) : \delta e(R)\mathrm{d}R$$

$$- \int \{R_1\cdot\delta\bar{\epsilon}(R_1) - R_2\cdot\delta\bar{\epsilon}(R_2)\}P(R_1)P(R_2) \vdots \mathbf{V}_1\mathbf{V}_1\mathbf{V}_1 \frac{1}{8\pi|R_1-R_2|}$$

$$\mathrm{d}R_1\,\mathrm{d}R_2. \quad (289)$$

This form for the change of the free energy seems to be dependent on the deformation tensor $\delta\boldsymbol{\epsilon}$ (or δe (A51)) throughout the volume. We may however obtain an alternative form of $\delta_\varepsilon F^*$ which shows explicitly that only the deformation at the surface comes into play. Such an expression follows if one employs (A48) of the third appendix. Together with (241) one then finds

$$\delta_\varepsilon F^* = -\int^S \boldsymbol{n}\cdot\mathbf{P}\cdot\delta\boldsymbol{\epsilon}\cdot R\,\mathrm{d}S - \tfrac{1}{2}\int^S \boldsymbol{n}\cdot\delta\boldsymbol{\epsilon}\cdot R(\mathbf{P}\cdot\boldsymbol{n})^2\mathrm{d}S. \quad (290)$$

(For uniform pressure and deformation tensors this formula reduces to (242).) One may prove the equivalence of (289) and (290) by performing a partial integration in the first term of (289), using the definition (A51) of δe, and employing the identity

$$\int (\mathbf{V}\cdot\mathbf{P})\cdot\delta\boldsymbol{\epsilon}\cdot R\,\mathrm{d}R + \tfrac{1}{2}\int^S \boldsymbol{n}\cdot\delta\boldsymbol{\epsilon}\cdot R(\mathbf{P}\cdot\boldsymbol{n})^2\mathrm{d}S$$

$$= \int \{R_1\cdot\delta\bar{\epsilon}(R_1) - R_2\cdot\delta\bar{\epsilon}(R_2)\}P(R_1)P(R_2) \vdots \mathbf{V}_1\mathbf{V}_1\mathbf{V}_1 \frac{1}{8\pi|R_1-R_2|}$$

$$\mathrm{d}R_1\,\mathrm{d}R_2, \quad (291)$$

which holds for a polarized system in equilibrium. The proof of this relation (v. problem 5) makes use of the equation of motion (150), which for the present system in equilibrium and at rest reads

$$\mathbf{V}\cdot\mathbf{P} = (\mathbf{V}E)\cdot\mathbf{P} + (\mathbf{V}B)\cdot\mathbf{M}. \quad (292)$$

In the second term at the right-hand side only the external magnetic field appears (v. (71)). This field is uniform, so that (292) reduces to

$$\mathbf{V}\cdot\mathbf{P} = (\mathbf{V}E)\cdot\mathbf{P}. \quad (293)$$

(For uniform pressure, deformation tensor and polarization the relation (291) reduces to (243), as follows by employing (236).)

The change of entropy is found now if one substitutes (227) and (289) or (290) into (279). In the latter case, i.e. with (290), we get the entropy law

$$T\delta S = \delta U^* + \int n \cdot P \cdot \delta \epsilon \cdot R \, dS + \tfrac{1}{2} \int^S n \cdot \delta \epsilon \cdot R (P \cdot n)^2 dS + V\bar{P} \cdot \delta E_e + V\bar{M} \cdot \delta B_e ,$$
(294)

while in the first case, i.e. with (289), the result is

$$T\delta S = \delta U^* + \int P(R) : \delta e(R) dR + \int \{R_1 \cdot \delta \tilde{\epsilon}(R_1) - R_2 \cdot \delta \tilde{\epsilon}(R_2)\} P(R_1) P(R_2)$$

$$: \nabla_1 \nabla_1 \nabla_1 \frac{1}{8\pi|R_1 - R_2|} dR_1 \, dR_2 + V\bar{P} \cdot \delta E_e + V\bar{M} \cdot \delta B_e . \quad (295)$$

The form (294) shows that the change of entropy depends only on the deformation tensor at the boundary, while (295) has a form that reduces for uniform pressure, deformation and polarizations to (244) of subsection *b*. If one inserts moreover (281) the relation (295) becomes

$$T\delta S = \delta U + \int P(R) : \delta e(R) dR - E_e \cdot \delta(V\bar{P})$$

$$- \delta \left\{ \int P(R_1) P(R_2) : \nabla_1 \nabla_1 \frac{1}{8\pi|R_1 - R_2|} dR_1 \, dR_2 \right\}$$

$$+ \int \{R_1 \cdot \delta \tilde{\epsilon}(R_1) - R_2 \cdot \delta \tilde{\epsilon}(R_2)\} P(R_1) P(R_2) : \nabla_1 \nabla_1 \nabla_1 \frac{1}{8\pi|R_1 - R_2|}$$

$$dR_1 \, dR_2 + V\bar{M} \cdot \delta B_e . \quad (296)$$

We may cast this law in a form which contains the Maxwell fields instead of the external fields. Let us consider the fourth term of the right-hand side separately. As a consequence of the variation the polarization changes and also the boundary of the integral, so that it may be written as

$$- \int [\{\delta_0 P(R_1)\} P(R_2) + P(R_1)\delta_0 P(R_2)] : \nabla_1 \nabla_1 \frac{1}{8\pi|R_1 - R_2|} dR_1 \, dR_2$$

$$- \int^V dS_1 \int^S dR_2 \, \delta R_1 \cdot n P(R_1) P(R_2) : \nabla_1 \nabla_1 \frac{1}{8\pi|R_1 - R_2|}$$

$$- \int^S dS_2 \int^V dR_1 \, \delta R_2 \cdot n P(R_1) P(R_2) : \nabla_1 \nabla_1 \frac{1}{8\pi|R_1 - R_2|} , \quad (297)$$

where in the first term $\delta_0 P(R_i)$ is the 'syntopic' variation (i.e. $P'(R_i) - P(R_i)$) of the polarization. In the second term the integration with respect to R_1 is

extended over the surface S of the sample with surface element dS_1 and normal n, while the integration with respect to R_2 is performed over the volume V. Furthermore δR_1 is the variation $\delta \epsilon(R_1) \cdot R_1$. Similar remarks apply to the third term. If the last two terms are transformed with Gauss's theorem we obtain for (297):

$$- \int [\{\delta P(R_1) P(R_2) + P(R_1)\delta P(R_2)\} : \nabla_1 \nabla_1$$

$$+ \{R_1 \cdot \delta \tilde{\epsilon}(R_1) - R_2 \cdot \delta \tilde{\epsilon}(R_2)\} P(R_1) P(R_2) : \nabla_1 \nabla_1 \nabla_1$$

$$+ \{\mathrm{Tr} \, \delta e(R_1) + \mathrm{Tr} \, \delta e(R_2)\} P(R_1) P(R_2) : \nabla_1 \nabla_1] \frac{1}{8\pi|R_1 - R_2|} dR_1 \, dR_2 ,$$
(298)

where the 'asyntopic' variations of the polarizations ($i = 1, 2$) are

$$\delta P(R_i) \equiv P'(R_i') - P(R_i) = \delta_0 P(R_i) + R_i \cdot \delta \tilde{\epsilon}(R_i) \cdot \nabla_i P(R_i). \quad (299)$$

The third term at the right-hand side of (296) may likewise be written in terms of the asyntopic variation (299) since

$$\delta(V\bar{P}) \equiv \delta \int P(R) dR = \int \delta P(R) dR + \int \{\mathrm{Tr} \, \delta e(R)\} P(R) dR. \quad (300)$$

Substituting (298) and (300) into (296), we obtain with the expressions (71) for the Maxwell fields (with vanishing charge density) the non-relativistic entropy law

$$T\delta S = \delta U + \int [P(R) : \delta e(R) - E(R) \cdot \delta P(R)$$

$$- \{\mathrm{Tr} \, \delta e(R)\} P(R) \cdot E(R) + M(R) \cdot \delta B] dR, \quad (301)$$

or with the bar notation for volume averages

$$T\delta S = \delta U + V\overline{P : \delta e} - V\overline{E \cdot \delta P} - V\overline{(\mathrm{Tr} \, \delta e)P \cdot E} + V\bar{M} \cdot \delta B. \quad (302)$$

This form of the entropy law is closely analogous to (247) if the latter is multiplied by the total (constant) mass M of the system (so that s, u and v are replaced by S, U and V). The difference between these formulae is that (302) contains the tensor δe instead of $\delta \epsilon$ and volume averages instead of uniform quantities.

The entropy law (301) or (302) contains the tensor $\delta e(R)$, which characterizes the deformation throughout the volume. However, one may show by a transformation of the right-hand side of (301) that effectively only values of the deformation tensor at the surface come in, just as in (289–290).

With the help of (A51), (299) and partial integrations one may write (301) as

$$T\delta S = \delta U + \int^S n\cdot(\mathbf{P}\cdot\delta\boldsymbol{\epsilon}\cdot R - \delta\boldsymbol{\epsilon}\cdot RP\cdot E)\mathrm{d}S$$

$$- \int \{(\nabla\cdot\mathbf{P})\cdot\delta\boldsymbol{\epsilon}\cdot R + E\cdot\delta_0 P - R\cdot\delta\tilde{\boldsymbol{\epsilon}}\cdot(\nabla E)\cdot P - M\cdot\delta_0 B\}\mathrm{d}R, \quad (303)$$

where n is the outward normal to the surface element $\mathrm{d}S$. We now substitute the equation of motion (293), with the result

$$T\delta S = \delta U + \int^S n\cdot(\mathbf{P}\cdot\delta\boldsymbol{\epsilon}\cdot R - \delta\boldsymbol{\epsilon}\cdot RP\cdot E)\mathrm{d}S - \int (E\cdot\delta_0 P - M\cdot\delta_0 B)\mathrm{d}R, \quad (304)$$

which may also be obtained directly from (294). This formula shows that the change of entropy depends only on the value at the surface of the deformation tensor $\delta\boldsymbol{\epsilon}$. It depends moreover on the variation of the total energy, of the polarization and of the magnetic field throughout the system.

It should be noted that the infinitesimal $\delta\boldsymbol{\epsilon}$ is defined by (225) and is thus not the variation of a state variable. Just as in subsection b let us introduce as state variables characterizing the deformation of the boundary a tensor $\hat{\boldsymbol{\eta}}$, which gives the transformation of the position R of the boundary from a fixed position $R°$ in a reference state denoted by the symbol $°$ to a deformed state

$$R = \hat{\boldsymbol{\eta}}(R°)\cdot R°. \quad (305)$$

(In contrast to the case of subsection b the tensor $\hat{\boldsymbol{\eta}}$ is now a function of $R°$.) For an infinitesimal deformation we have then

$$\delta R = \delta\hat{\boldsymbol{\eta}}(R°)\cdot R° = \delta\hat{\boldsymbol{\eta}}(R°)\cdot\hat{\boldsymbol{\eta}}^{-1}(R°)\cdot R, \quad (306)$$

so that the variation $\delta\boldsymbol{\epsilon}(R)$ is

$$\delta\boldsymbol{\epsilon}(R) = \delta\hat{\boldsymbol{\eta}}(R°)\cdot\hat{\boldsymbol{\eta}}^{-1}(R°). \quad (307)$$

We want to write the tensor $\hat{\boldsymbol{\eta}}(R°)$ as the product of an orthogonal tensor $\boldsymbol{\eta}_A$ (independent of $R°$) and a tensor $\boldsymbol{\eta}(R°)$. To fix $\boldsymbol{\eta}_A$ we factorize the surface integral

$$\int^{S°} \hat{\boldsymbol{\eta}}(R°)\cdot R°n°\mathrm{d}S° \quad (308)$$

(where $n°$ is the normal to the surface element $\mathrm{d}S°$ of the surface $S°$ in the reference state) into a product of the orthogonal tensor $\boldsymbol{\eta}_A$ and a symmetric tensor. This condition fixes the tensor $\boldsymbol{\eta}_A$. With the help of $\boldsymbol{\eta}_A$ we now define $\boldsymbol{\eta}(R°)$ by means of the relation

$$\hat{\boldsymbol{\eta}}(R°) = \boldsymbol{\eta}_A\cdot\boldsymbol{\eta}(R°). \quad (309)$$

In view of (308) the tensor $\boldsymbol{\eta}(R°)$ has the property that

$$\int^{S°} \boldsymbol{\eta}(R°)\cdot R°n°\mathrm{d}S° \quad (310)$$

is symmetric.

The reason for factorizing the tensor $\hat{\boldsymbol{\eta}}$ in the particular way described above is that a rotation of the body as a whole without deformations is described by a change of $\boldsymbol{\eta}_A$, leaving $\boldsymbol{\eta}(R°)$ invariant. (From (310) it is apparent that if $\boldsymbol{\eta}(R°)$ is uniform over the surface, then this tensor $\boldsymbol{\eta}$ is itself symmetric.)

If the sample is only slightly deformable the tensor $\boldsymbol{\eta}(R°)$ is nearly equal to the unit tensor $\mathbf{U}$. Introducing (309) into (307) we get for the variation $\delta\boldsymbol{\epsilon}$:

$$\delta\boldsymbol{\epsilon}(R) = \{\delta\boldsymbol{\eta}_A\cdot\boldsymbol{\eta}(R°) + \boldsymbol{\eta}_A\cdot\delta\boldsymbol{\eta}(R°)\}\cdot\boldsymbol{\eta}^{-1}(R°)\cdot\boldsymbol{\eta}_A^{-1} \simeq \delta\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A + \boldsymbol{\eta}_A\cdot\delta\boldsymbol{\eta}(\tilde{\boldsymbol{\eta}}_A\cdot R)\cdot\tilde{\boldsymbol{\eta}}_A, \quad (311)$$

where in the second expression $\boldsymbol{\eta}(R°)$ could be replaced by the unit tensor and $\delta\boldsymbol{\eta}(R°)$ by $\delta\boldsymbol{\eta}(\tilde{\boldsymbol{\eta}}_A\cdot R)$ as a consequence of the fact that the deformations are small. The first term in the last member of (311) is antisymmetric as follows from the orthogonality of $\boldsymbol{\eta}_A$. With the help of (304) we obtain for the change of entropy

$$T\delta S = \delta U + \int^S n\cdot(\mathbf{P} - P\cdot E\mathbf{U})\cdot\delta\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A\cdot R\,\mathrm{d}S$$

$$+ \int^S n\cdot(\mathbf{P} - P\cdot E\mathbf{U})\cdot\boldsymbol{\eta}_A\cdot\delta\boldsymbol{\eta}(\tilde{\boldsymbol{\eta}}_A\cdot R)\cdot\tilde{\boldsymbol{\eta}}_A\cdot R\,\mathrm{d}S - \int(E\cdot\delta_0 P - M\cdot\delta_0 B)\mathrm{d}R, \quad (312)$$

where the quantities $\mathbf{P}$, E, B, P and M all depend on the space coordinates R. With the use of Gauss's theorem and (293) the first integral at the right-hand side may be transformed, so that one gets

$$T\delta S = \delta U + \int \mathbf{P} : (\delta\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A)\mathrm{d}R$$

$$+ \int^S n\cdot(\mathbf{P} - P\cdot E\mathbf{U})\cdot\boldsymbol{\eta}_A\cdot\delta\boldsymbol{\eta}(\tilde{\boldsymbol{\eta}}_A\cdot R)\cdot\tilde{\boldsymbol{\eta}}_A\cdot R\,\mathrm{d}S - \int(E\cdot\delta_A P - M\cdot\delta_A B)\mathrm{d}R, \quad (313)$$

where we used the fact that the trace of $\delta\boldsymbol{\eta}_A\cdot\tilde{\boldsymbol{\eta}}_A$ vanishes, and the notation

$$\delta_A \equiv \delta_0 + R\cdot\boldsymbol{\eta}_A\cdot\delta\tilde{\boldsymbol{\eta}}_A\cdot\nabla. \quad (314)$$

In the second term at the right-hand side of (313) only the antisymmetrical part $\frac{1}{2}(\mathbf{P} - \tilde{\mathbf{P}})$ of the pressure tensor contributes, because the other factor is antisymmetric. It follows from the angular balance equation (196) (cf. sub-

section 6*d*) by integration over the volume that

$$\int P_A \, dR = \int (P \wedge E + M \wedge B) \, dR \qquad (315)$$

as a consequence of the fact that the system is in equilibrium and at rest. Alternatively one may write

$$\int \tfrac{1}{2}(P - \tilde{P}) \, dR = \int \tfrac{1}{2}(PE - EP + MB - BM) \, dR. \qquad (316)$$

Substituting this relation into (313) we get the entropy law

$$T \delta S = \delta U + \int^S n \cdot (P - P \cdot EU) \cdot \eta_A \cdot \delta \eta(\tilde{\eta}_A \cdot R) \cdot \tilde{\eta}_A \cdot R \, dS$$
$$- \int \{ E \cdot \delta_A P - M \cdot \delta_A B - (PE + MB) : (\delta \eta_A \cdot \tilde{\eta}_A) \} dR, \quad (317)$$

which gives the entropy in its dependence on the change of the total internal energy, of the electric polarization, the magnetic field and the state variables η_A and $\eta(\tilde{\eta}_A \cdot R)$ at the surface.

In the case that the solid is not rotated but only deformed, the entropy law (317) reduces to

$$T \delta S = \delta U + \int^S n \cdot (P - P \cdot EU) \cdot \delta \eta(R) \cdot R \, dS - \int (E \cdot \delta_0 P - M \cdot \delta_0 B) dR, \qquad (318)$$

since then $\eta_A = U$.

In certain cases the polarizations in a system with long range correlations in a uniform external field are approximately uniform if the sample has ellipsoidal shape. This is indeed only an approximation, since not all physical quantities are uniform (the pressure tensor, for instance, will in general vary over the sample, cf. section 8*b*). In that case the entropy law (317) becomes

$$T dS = dU + \int^S n \cdot P(R) \cdot \eta_A \cdot d\eta(\tilde{\eta}_A \cdot R) \cdot \tilde{\eta}_A \cdot R \, dS + V(PE + MB) : (d\eta_A \cdot \tilde{\eta}_A)$$
$$- P \cdot E \int^S n \cdot \eta_A \cdot d\eta(\tilde{\eta}_A \cdot R) \cdot \tilde{\eta}_A \cdot R \, dS - VE \cdot dP + VM \cdot dB, \qquad (319)$$

which has been written with differentials since now all quantities are state variables. The fourth term at the right-hand side is equal to $-P \cdot E \, dV$ as follows from (225), (311), Gauss's theorem and the fact that $d\eta_A \cdot \tilde{\eta}_A$ is traceless. Therefore (319) becomes

$$T dS = dU + \int^S n \cdot P(R) \cdot \eta_A \cdot d\eta(\tilde{\eta}_A \cdot R) \cdot \tilde{\eta}_A \cdot R \, dS$$
$$+ V(PE + MB) : (d\eta_A \cdot \tilde{\eta}_A) - E \cdot d(VP) + VM \cdot dB. \qquad (320)$$

In the case that no rotations of the solid are considered this relation reduces to

$$T dS = dU + \int^S n \cdot P(R) \cdot d\eta(R) \cdot R \, dS - E \cdot d(VP) + VM \cdot dB, \qquad (321)$$

since then $\eta_A = U$ (it also follows from (318) as a special case)[1]. The set of integrability conditions includes the relations between polarizations and fields ($i, j = 1, 2, 3$)

$$\frac{\partial P_i}{\partial E_j} = \frac{\partial P_j}{\partial E_i}, \qquad \frac{\partial P_i}{\partial B_j} = \frac{\partial M_j}{\partial E_i}, \qquad \frac{\partial M_i}{\partial B_j} = \frac{\partial M_j}{\partial B_i}, \qquad (322)$$

where the polarizations have been considered as functions of E, B, T or S, and η. (These relations are trivially valid for isotropic substances.)

The Gibbs relation (320–321), which is an approximation to the entropy law (317–318), is the final result for crystalline solids. It shows how the total entropy is a function of the total energy, the polarization, the magnetic field and the deformation tensor at the boundary. The law is the counterpart of the Gibbs relations (251) for fluids and (260) for amorphous or polycrystalline solids. In contrast to these local laws the result just found has the form of a global law: it makes no sense to subdivide a crystalline solid (in which long range correlations are present) into nearly uniform cells for which local laws may be derived.

e. *The entropy balance equation*

For fluid systems of neutral atoms we found a first law of the form (211) and a second law of the form (251). The latter equation has been derived for a system at rest so that the fields and polarizations are measured in the rest

[1] In (321) the complete pressure tensor P appears. If the tensor $d\eta(R)$ is uniform over the surface, it follows from (310) that it is symmetric. With the help of Gauss's theorem, (293) and the uniformity of the electric field E one may write then the second term at the right-hand side of (321) as $(\int P(R) dR) : d\eta$. Since now $d\eta$ is symmetric only the symmetric part of the pressure tensor comes into play. The same statement may be made for another special case, namely that of a pressure tensor which is uniform over the surface. In that case it follows directly from (310) that the second term at the right-hand side of (321) contains only the symmetric part of this uniform pressure tensor. Similar remarks apply to the corresponding terms in (320).

frame. They are therefore the same as those occurring in (211). The second law, which we may write as

$$\varrho \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\varrho}{T} \frac{\mathrm{d}u}{\mathrm{d}t} + \frac{\varrho}{T} p \frac{\mathrm{d}v}{\mathrm{d}t} - \frac{\varrho}{T} \boldsymbol{E}' \cdot \frac{\mathrm{d}(v\boldsymbol{P}')}{\mathrm{d}t} + \frac{1}{T} \boldsymbol{M}' \cdot \frac{\mathrm{d}\boldsymbol{B}'}{\mathrm{d}t}, \qquad (323)$$

is supposed to be valid also for fluid systems which are not too far from equilibrium. If we substitute the first law (211) into this equation we obtain the balance of entropy

$$\varrho \frac{\mathrm{d}s}{\mathrm{d}t} = -\boldsymbol{\nabla} \cdot \left(\frac{\boldsymbol{J}_q}{T} \right) - \frac{\boldsymbol{J}_q}{T^2} \cdot \boldsymbol{\nabla} T - \frac{1}{T} (\tilde{\boldsymbol{P}} - p\mathrm{U}) : \boldsymbol{\nabla}v, \qquad (324)$$

where we used mass conservation in the form $\varrho \mathrm{d}v/\mathrm{d}t = \boldsymbol{\nabla} \cdot v$, as follows from (59) and (159). This balance equation shows that the entropy changes as the result of the divergence of an entropy (conduction) flow $\boldsymbol{J}_q/T$ and an entropy source strength arising from heat conduction and viscous phenomena. In equilibrium the source term vanishes since the temperature and velocity fields are then uniform. (Moreover simultaneously the heat flow $\boldsymbol{J}_q$ and the viscous pressure $\boldsymbol{P} - p\mathrm{U}$ also vanish then.) Outside equilibrium the entropy source strength is positive, as may be shown if the distribution function is known to satisfy particular equations, like Boltzmann's.

In the preceding we assumed that the quantities $\boldsymbol{E}'$ and $\boldsymbol{M}'$ in (211) were equal to the equilibrium values $\boldsymbol{E}'_{\mathrm{eq}}$ and $\boldsymbol{M}'_{\mathrm{eq}}$ of these quantities occurring in (323), so that in the entropy source strength no electromagnetic contributions appear. If however $\boldsymbol{E}'$ and $\boldsymbol{M}'$ are supposed different from their equilibrium values we obtain instead of (324) as the balance of entropy:

$$\varrho \frac{\mathrm{d}s}{\mathrm{d}t} = -\boldsymbol{\nabla} \cdot \left(\frac{\boldsymbol{J}_q}{T} \right) - \frac{\boldsymbol{J}_q}{T^2} \cdot \boldsymbol{\nabla} T - \frac{1}{T} (\tilde{\boldsymbol{P}} - p\mathrm{U}) : \boldsymbol{\nabla}v$$

$$+ \frac{\varrho}{T} (\boldsymbol{E}' - \boldsymbol{E}'_{\mathrm{eq}}) \cdot \frac{\mathrm{d}(v\boldsymbol{P}')}{\mathrm{d}t} - \frac{1}{T} (\boldsymbol{M}' - \boldsymbol{M}'_{\mathrm{eq}}) \cdot \frac{\mathrm{d}\boldsymbol{B}'}{\mathrm{d}t} . \qquad (325)$$

The last two terms show which contributions to the entropy production arise from electromagnetic phenomena. They represent the entropy source strength due to electric and magnetic relaxation.

For amorphous and polycrystalline solids the first law (211) may be written in a slightly different form if one uses the relation

$$\boldsymbol{\nabla}v = \boldsymbol{\nabla} \left(\frac{\mathrm{d}\boldsymbol{\epsilon}}{\mathrm{d}t} \cdot \boldsymbol{R} \right) = \frac{\mathrm{d}\tilde{\boldsymbol{\epsilon}}}{\mathrm{d}t}, \qquad (326)$$

as follows from the definition (225) of the uniform deformation tensor $\delta\boldsymbol{\epsilon}$.

Inserting this expression we then find:

$$\varrho \frac{\mathrm{d}u}{\mathrm{d}t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_q - \boldsymbol{P} : \frac{\mathrm{d}\boldsymbol{\epsilon}}{\mathrm{d}t} + \varrho \frac{\mathrm{d}v\boldsymbol{P}'}{\mathrm{d}t} \cdot \boldsymbol{E}' - \boldsymbol{M}' \cdot \frac{\mathrm{d}\boldsymbol{B}'}{\mathrm{d}t} . \qquad (327)$$

If this relation is combined with the entropy law (260) (which will be assumed to be valid in the neighbourhood of equilibrium) written as

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\varrho}{T} \frac{\mathrm{d}u}{\mathrm{d}t} + \frac{1}{T} \boldsymbol{P}_{\mathrm{eq}} : \frac{\mathrm{d}\boldsymbol{\epsilon}}{\mathrm{d}t} - \frac{\varrho}{T} \boldsymbol{E}' \cdot \frac{\mathrm{d}(v\boldsymbol{P}')}{\mathrm{d}t} + \frac{1}{T} \boldsymbol{M}' \cdot \frac{\mathrm{d}\boldsymbol{B}'}{\mathrm{d}t}, \qquad (328)$$

with a symmetric equilibrium pressure, one gets an entropy balance which has the same form as (325) but for the third term at the right-hand side, which reads now

$$-\frac{1}{T} (\boldsymbol{P} - \boldsymbol{P}_{\mathrm{eq}}) : \frac{\mathrm{d}\boldsymbol{\epsilon}}{\mathrm{d}t} . \qquad (329)$$

For a neutral plasma the first law of thermodynamics has been given in (216) and the second law in (276). For a plasma not too far from equilibrium one obtains the entropy balance equation

$$\varrho \frac{\mathrm{d}s}{\mathrm{d}t} = -\boldsymbol{\nabla} \cdot \left(\frac{\boldsymbol{J}_q}{T} \right) - \frac{\boldsymbol{J}_q}{T^2} \cdot \boldsymbol{\nabla} T - \frac{1}{T} (\tilde{\boldsymbol{P}} - p\mathrm{U}) : \boldsymbol{\nabla}v + \frac{1}{T} \boldsymbol{J} \cdot \boldsymbol{E}', \qquad (330)$$

where the last term represents the entropy source due to Joule heat produced in the plasma.

Since for systems with long range correlations only a global entropy law has been derived, it is not possible to find a local entropy balance equation in the same way as above. The global entropy production law will follow by combining the first and second laws, both in their global forms. The global form of the first law is a direct consequence of (217) with (212). In fact, integrating (217) over the mass of the system, one finds

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}U}{\mathrm{d}t} + \int \left\{ \tilde{\boldsymbol{P}} : \boldsymbol{\nabla}v - \boldsymbol{J}' \cdot \boldsymbol{E}' - \varrho \frac{\mathrm{d}(v\boldsymbol{P}')}{\mathrm{d}t} \cdot \boldsymbol{E}' + \boldsymbol{M}' \cdot \frac{\mathrm{d}\boldsymbol{B}'}{\mathrm{d}t} \right\} \mathrm{d}R \qquad (331)$$

with the amount of heat added to the system per unit of time

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\int \boldsymbol{J}_q \cdot \boldsymbol{n} \, \mathrm{d}S. \qquad (332)$$

Now one has for a non-uniform solid system (cf. (326)):

$$\boldsymbol{\nabla}v = \boldsymbol{\nabla} \left(\frac{\mathrm{d}\boldsymbol{\epsilon}}{\mathrm{d}t} \cdot \boldsymbol{R} \right) = \frac{\mathrm{d}\tilde{\boldsymbol{\epsilon}}}{\mathrm{d}t}, \qquad (333)$$

as follows from (225) and (A51). With this relation (331) becomes

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}U}{\mathrm{d}t} + \int \left\{ \mathbf{P} : \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}t} - \mathbf{J}' \cdot \mathbf{E}' - \varrho \frac{\mathrm{d}(v\mathbf{P}')}{\mathrm{d}t} \cdot \mathbf{E}' + \mathbf{M}' \cdot \frac{\mathrm{d}\mathbf{B}'}{\mathrm{d}t} \right\} \mathrm{d}R. \quad (334)$$

This form of the first law is to be compared with the entropy law (301). In the latter we divide by δt. Then it becomes

$$T\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}U}{\mathrm{d}t} + \int \left\{ \mathbf{P} : \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}t} - \mathbf{E}' \cdot \frac{\mathrm{d}\mathbf{P}'}{\mathrm{d}t} - \left(\mathrm{Tr}\, \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}t} \right) \mathbf{P}' \cdot \mathbf{E}' + \mathbf{M}' \cdot \frac{\mathrm{d}\mathbf{B}'}{\mathrm{d}t} \right\} \mathrm{d}R. \quad (335)$$

At the right-hand side we added primes to indicate that the quantities are taken in the rest frame (the second law has been derived for a system at rest). Using the fact that, as a consequence of (333) $\mathrm{Tr}\,(\mathrm{d}\mathbf{e}/\mathrm{d}t)$ is equal to $\nabla \cdot v$ or to $\varrho\,\mathrm{d}v/\mathrm{d}t$ with $v = \varrho^{-1}$ the specific volume (as follows from the conservation of mass), one may write (335) in the form:

$$T\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}U}{\mathrm{d}t} + \int \left\{ \mathbf{P} : \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}t} - \varrho \frac{\mathrm{d}(v\mathbf{P}')}{\mathrm{d}t} \cdot \mathbf{E}' + \mathbf{M}' \cdot \frac{\mathrm{d}\mathbf{B}'}{\mathrm{d}t} \right\} \mathrm{d}R. \quad (336)$$

Again we assume that this law remains valid if the system is near equilibrium. Then one finds, by combining (334) and (336), for the global entropy balance equation

$$T\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t} - \int \left\{ (\mathbf{P} - \mathbf{P}_{\mathrm{eq}}) : \frac{\mathrm{d}\mathbf{e}}{\mathrm{d}t} - \varrho \frac{\mathrm{d}(v\mathbf{P}')}{\mathrm{d}t} \cdot (\mathbf{E}' - \mathbf{E}'_{\mathrm{eq}}) + (\mathbf{M}' - \mathbf{M}'_{\mathrm{eq}}) \cdot \frac{\mathrm{d}\mathbf{B}'}{\mathrm{d}t} \right\} \mathrm{d}R, \quad (337)$$

where we added some indices eq to distinguish the equilibrium values, occurring in the second law, from the non-equilibrium values occurring in the first law. Note that the temperature has been supposed to be uniform, so that no term with the gradient of the temperature appears in (337), in contrast with what was the case in (325). At the right-hand side of (337) appears, apart from a term with the supplied heat, a volume integral which contains elastic, electric and magnetic relaxation terms.

A particular case, which arises for ferromagnetic materials, is that of a system in which magnetic hysteresis occurs. If one considers a cyclic process, in which no elastic after-effects occur, we have, if no heat is added,

$$T\Delta S = - \int \oint (\mathbf{M}' - \mathbf{M}'_{\mathrm{eq}}) \cdot \mathrm{d}\mathbf{B}' \, \mathrm{d}R \quad (338)$$

for the entropy production ΔS per cycle.

8   Helmholtz and Kelvin forces

a. Fluids

Let us consider a fluid of neutral atoms in which constitutive relations exist between the polarizations and fields:

$$\begin{aligned} \mathbf{P}' &= \kappa(v, T)\mathbf{E}', \\ \mathbf{M}' &= \chi(v, T)\mathbf{B}'. \end{aligned} \quad (339)$$

Primes have been added to indicate that the quantities are counted in the rest frame. The electric and magnetic susceptibilities κ and χ depend on the specific volume v and the temperature T. The second law for such a fluid in local equilibrium has been given in (251) and may be written in the form

$$\mathrm{d}f = -p\,\mathrm{d}v - s\,\mathrm{d}T + \mathbf{E}' \cdot \mathrm{d}(v\mathbf{P}') - v\mathbf{M}' \cdot \mathrm{d}\mathbf{B}' \quad (340)$$

with the specific free energy

$$f = u - Ts. \quad (341)$$

The differential expression (340) may be integrated at constant specific volume and temperature. Then one finds for the difference of the specific free energy in the presence and that in the absence of fields:

$$f - f_0 = v \int (\mathbf{E}' \cdot \mathrm{d}\mathbf{P}' - \mathbf{M}' \cdot \mathrm{d}\mathbf{B}'). \quad (342)$$

With (339) this relation becomes

$$f - f_0 = \tfrac{1}{2} v (\mathbf{P}' \cdot \mathbf{E}' - \mathbf{M}' \cdot \mathbf{B}'). \quad (343)$$

The scalar equilibrium pressure follows from the specific free energy by differentiation with respect to the specific volume at constant temperature, specific polarization $v\mathbf{P}'$ and magnetic field $\mathbf{B}'$, as (340) shows. Hence the pressure $p = -\partial f / \partial v$ is connected to the pressure $p_0 = -\partial f_0 / \partial v$ for the same values of v and T, but with switched-off fields by a relation[1] which follows from (343):

$$p - p_0 = \frac{1}{2} \left(\mathbf{P}' \cdot \mathbf{E}' + \mathbf{M}' \cdot \mathbf{B}' + v \frac{\partial \kappa}{\partial v} E'^2 + v \frac{\partial \chi}{\partial v} B'^2 \right). \quad (344)$$

The specific entropy follows from the specific free energy by differentiation with respect to temperature T at constant v, $v\mathbf{P}'$ and $\mathbf{B}'$. From (343) one has

$$s - s_0 = -\frac{1}{2} \left(v \frac{\partial \kappa}{\partial T} E'^2 + v \frac{\partial \chi}{\partial T} B'^2 \right), \quad (345)$$

[1] P. Mazur and I. Prigogine, Mém. Acad. Roy. Belg. (Cl. Sc.) **28**(1953)fasc. 1; cf. W. F. Brown jr., Am. J. Phys. **19**(1951)290, 333.

so that the difference of the specific energies is

$$u - u_0 = \tfrac{1}{2}v \left(\mathbf{P}' \cdot \mathbf{E}' - \mathbf{M}' \cdot \mathbf{B}' + T \frac{\partial \kappa}{\partial T} E'^2 + T \frac{\partial \chi}{\partial T} B'^2 \right), \qquad (346)$$

as follows from (343) with (341).

The relation (344) shows how the pressure changes if the fields are switched on. The pressure p is the equilibrium value of the pressure $\mathbf{P}$ used so far. We shall call it the Kelvin pressure, to distinguish it from the pressure p_0, defined at equilibrium and with switched-off fields. The latter will be called the Helmholtz pressure at that specific volume and temperature.

In the equation of motion for a fluid of neutral atoms, which has been given in (105) with (106) or in (158), we introduce the Helmholtz pressure instead of the Kelvin pressure by using (344). Then we obtain

$$\varrho \frac{d\boldsymbol{v}}{dt} = -\nabla p_0 - \nabla \cdot \boldsymbol{\Pi} + (\nabla \mathbf{E}) \cdot \mathbf{P} + (\nabla \mathbf{B}) \cdot \mathbf{M}$$

$$+ c^{-1} \varrho \frac{d}{dt} (v\mathbf{P} \wedge \mathbf{B}) - \tfrac{1}{2} \nabla \left(\mathbf{P}' \cdot \mathbf{E}' + \mathbf{M}' \cdot \mathbf{B}' + v \frac{\partial \kappa}{\partial v} E'^2 + v \frac{\partial \chi}{\partial v} B'^2 \right), \quad (347)$$

where the viscous pressure tensor

$$\boldsymbol{\Pi} \equiv \mathbf{P} - p\mathbf{U} \qquad (348)$$

has been introduced. Alternatively, introducing rest frame quantities with the help of (26) and (27), we have for the equation of motion, using also (339)

$$\varrho \frac{d\boldsymbol{v}}{dt} = -\nabla p_0 - \nabla \cdot \boldsymbol{\Pi} + \mathscr{F}, \qquad (349)$$

where the 'Helmholtz' force density is:

$$\mathscr{F} \equiv -\frac{1}{2} \left\{ E'^2 \nabla \kappa + B'^2 \nabla \chi + \nabla \left(v \frac{\partial \kappa}{\partial v} E'^2 + v \frac{\partial \chi}{\partial v} B'^2 \right) \right\} + c^{-1} (\nabla v) \cdot (\mathbf{P}' \wedge \mathbf{B}')$$

$$+ c^{-1} \varrho \frac{d}{dt} (v\mathbf{P}' \wedge \mathbf{B}') + (\nabla \mathbf{E}') \cdot (\mathbf{P}' - \mathbf{P}'_{eq}) + (\nabla \mathbf{B}') \cdot (\mathbf{M}' - \mathbf{M}'_{eq}). \qquad (350)$$

Here $\mathbf{P}'_{eq}$ and $\mathbf{M}'_{eq}$ represent the equilibrium values (339) in the rest frame.

The Helmholtz force $\mathscr{F}$ has a simpler form in the important special case of fluids in equilibrium and at rest in time-independent fields. Then the expression (350) reduces to

$$\mathscr{F} = -\frac{1}{2} \left\{ E'^2 \nabla \kappa + B'^2 \nabla \chi + \nabla \left(v \frac{\partial \kappa}{\partial v} E'^2 + v \frac{\partial \chi}{\partial v} B'^2 \right) \right\}. \qquad (351)$$

The equation of motion reduces under these circumstances to

$$\mathscr{F} = \nabla p_0. \qquad (352)$$

The expression (351) contains the Helmholtz terms found on the basis of energy considerations[1]. The expression for static electric dipole systems has been derived already in a statistical treatment[2]. Earlier the connexion between Kelvin and Helmholtz forces and pressures had been found from thermodynamics[3].

Often one employs a magnetic susceptibility $\tilde{\chi}$ defined by

$$\mathbf{M}' = \tilde{\chi}(v, T)\mathbf{H}' \qquad (353)$$

instead of the second line of (339). The connexion between the two susceptibilities is then

$$\tilde{\chi} = \frac{\chi}{1 - \chi}. \qquad (354)$$

With the help of this relation one may eliminate χ in favour of $\tilde{\chi}$ in the relations (344–346) and in (347), (350) and (351). The latter becomes in particular

$$\mathscr{F} = -\frac{1}{2} \left\{ E'^2 \nabla \kappa + H'^2 \nabla \tilde{\chi} + \nabla \left(v \frac{\partial \kappa}{\partial v} E'^2 + v \frac{\partial \tilde{\chi}}{\partial v} H'^2 \right) \right\}. \qquad (355)$$

For practical applications one may alternatively use the equation of motion (105–106), which contains the Kelvin pressure and the Kelvin force, or the equation of motion (349–350), which has been written in terms of the Helmholtz pressure and the Helmholtz force. However the latter has a more limited validity, since it may only be employed if the system is characterized by linear constitutive relations. In its form (351–352) it may be applied only to equilibrium situations.

From the equation of motion (352) with (351) for a fluid in equilibrium and at rest, one may obtain the density distribution that arises if a static electromagnetic field is switched on. In fact since the Helmholtz pressure p_0 is a function of the density $\varrho = v^{-1}$ and the temperature T, one may write (352)

[1] D. J. Korteweg, Ann. Phys. Chem. 9(1880)48; H. von Helmholtz, Ann. Phys. Chem. 13(1881)385.

[2] P. Mazur and S. R. de Groot, Physica 22(1956)657.

[3] P. Mazur and I. Prigogine, op. cit. For a review and applications see S. R. de Groot and P. Mazur, Non-equilibrium thermodynamics (North-Holland Publ. Co., Amsterdam 1962); A. Sanfeld, Introduction to the thermodynamics of charged and polarized layers (Wiley, London 1968).

with (351) as

$$\mathbf{V}p_0 = \tfrac{1}{2}\varrho \mathbf{V}\left(\frac{\partial \kappa}{\partial \varrho}\,\boldsymbol{E}'^2 + \frac{\partial \chi}{\partial \varrho}\,\boldsymbol{B}'^2\right) \tag{356}$$

for constant T. If one defines now a function φ as

$$\varphi(p_0, T) = \int_{\bar{p}_0}^{p_0} \varrho^{-1}(\hat{p}_0, T)\mathrm{d}\hat{p}_0, \tag{357}$$

which follows from the equation of state $\varrho = \varrho(p_0, T)$ (the lower limit is an arbitrary, but fixed constant), one may write (356) as

$$\varphi(p_0, T) - \frac{1}{2}\frac{\partial \kappa}{\partial \varrho}\,\boldsymbol{E}'^2 - \frac{1}{2}\frac{\partial \chi}{\partial \varrho}\,\boldsymbol{B}'^2 = \text{const.,} \tag{358}$$

i.e. independent of the position in the fluid.

For an incompressible liquid at uniform temperature the function $\varphi(p_0, T)$ is equal to $v(p_0 - \bar{p}_0)$ with constant $v(T)$. Then one finds from (358)

$$p_0(\boldsymbol{R}) = p_0(\boldsymbol{R}_0) + \tfrac{1}{2}\varrho\left\{\frac{\partial \kappa}{\partial \varrho}\,\boldsymbol{E}'^2(\boldsymbol{R}) + \frac{\partial \chi}{\partial \varrho}\,\boldsymbol{B}'^2(\boldsymbol{R})\right\}, \tag{359}$$

where $\boldsymbol{R}_0$ denotes a position in the liquid where the fields vanish. Combining this result with the relation (344) between the Kelvin and Helmholtz pressures, one finds for the Kelvin pressure in an incompressible liquid at constant temperature

$$p(\boldsymbol{R}) = p_0(\boldsymbol{R}_0) + \tfrac{1}{2}\{\boldsymbol{P}'(\boldsymbol{R})\cdot\boldsymbol{E}'(\boldsymbol{R}) + \boldsymbol{M}'(\boldsymbol{R})\cdot\boldsymbol{B}'(\boldsymbol{R})\}. \tag{360}$$

An alternative way to derive this formula starts from the equation of motion (105–106), which may be written for the present case of a fluid in equilibrium and at rest

$$\mathbf{V}p = \tfrac{1}{2}\mathbf{V}(\boldsymbol{P}'\cdot\boldsymbol{E}' + \boldsymbol{M}'\cdot\boldsymbol{B}') + c^{-1}\frac{\partial}{\partial t}(\boldsymbol{P}' \wedge \boldsymbol{B}') - \tfrac{1}{2}(\boldsymbol{E}'^2\mathbf{V}\kappa + \boldsymbol{B}'^2\mathbf{V}\chi). \tag{361}$$

For an incompressible liquid at constant temperature the last terms vanish, so that one recovers for the static case (360).

If the dependence of the susceptibilities on the density is given by the Clausius–Mossotti laws

$$\frac{\kappa}{\kappa + 3} \sim \varrho, \qquad \frac{\chi}{3 - 2\chi} \sim \varrho, \tag{362}$$

one has for the partial derivatives

$$\varrho\,\frac{\partial \kappa}{\partial \varrho} = \kappa + \tfrac{1}{3}\kappa^2,$$
$$\varrho\,\frac{\partial \chi}{\partial \varrho} = \chi - \tfrac{2}{3}\chi^2. \tag{363}$$

If one inserts these relations into (359) one obtains

$$p_0(\boldsymbol{R}) = p_0(\boldsymbol{R}_0) + \tfrac{1}{2}\{\boldsymbol{P}'(\boldsymbol{R})\cdot\boldsymbol{E}'_{\mathrm{L}}(\boldsymbol{R}) + \boldsymbol{M}'(\boldsymbol{R})\cdot\boldsymbol{B}'_{\mathrm{L}}(\boldsymbol{R})\} \tag{364}$$

with the Lorentz cavity fields

$$\boldsymbol{E}'_{\mathrm{L}} \equiv \boldsymbol{E}' + \tfrac{1}{3}\boldsymbol{P}', \qquad \boldsymbol{B}'_{\mathrm{L}} \equiv \boldsymbol{B}' - \tfrac{2}{3}\boldsymbol{M}'. \tag{365}$$

For the electric case the relation (364) has been checked experimentally by measuring the index of refraction of a liquid placed between the plates of a condensor, which gives the pressures $p_0(\boldsymbol{R})$ and $p_0(\boldsymbol{R}_0)$ [1].

For an ideal gas the equation of state has the Boyle–Gay-Lussac form

$$\varrho = mp_0/kT \tag{366}$$

with m the mass of the molecules and k Boltzmann's constant. Then the function φ becomes

$$\varphi(p_0, T) = \frac{kT}{m}\log\frac{p_0}{\bar{p}_0}. \tag{367}$$

Inserting this into (358) one finds

$$\frac{\varrho(\boldsymbol{R})}{\varrho(\boldsymbol{R}_0)} = \frac{p_0(\boldsymbol{R})}{p_0(\boldsymbol{R}_0)} = \exp\left\{\frac{m}{2kT}\left(\frac{\partial \kappa}{\partial \varrho}\,\boldsymbol{E}'^2 + \frac{\partial \chi}{\partial \varrho}\,\boldsymbol{B}'^2\right)\right\}, \tag{368}$$

where at the right-hand side the quantities depend on $\boldsymbol{R}$. With (363) and (365) this relation reduces to

$$\frac{\varrho(\boldsymbol{R})}{\varrho(\boldsymbol{R}_0)} = \exp\left\{\frac{m}{2\varrho kT}\,(\boldsymbol{P}'\cdot\boldsymbol{E}'_{\mathrm{L}} + \boldsymbol{M}'\cdot\boldsymbol{B}'_{\mathrm{L}})\right\}. \tag{369}$$

This formula shows that the quantity $-(m/2\varrho)(\boldsymbol{P}'\cdot\boldsymbol{E}'_{\mathrm{L}} + \boldsymbol{M}'\cdot\boldsymbol{B}'_{\mathrm{L}})$ may be looked upon as the energy of a particle with an electric and a magnetic dipole moment in a field.

A useful application of the expression (360) arises if one considers a solid body at rest immersed in an incompressible liquid at uniform tempera-

[1] S. S. Hakim and J. B. Higham, Proc. Phys. Soc. 80(1962)190.

ture. In equilibrium the equation of motion (150) with (108) gives upon integration over a volume with a boundary that lies just outside the solid:

$$M\frac{\mathrm{d}v}{\mathrm{d}t} = -\int \{p\mathsf{U} - E'D' - H'B' + (\tfrac{1}{2}E'^2 + \tfrac{1}{2}B'^2 - M'\cdot B')\mathsf{U}\}\cdot n\,\mathrm{d}S, \quad (370)$$

where M is the total mass of the solid. If one employs now (360) one obtains the equation

$$M\frac{\mathrm{d}v}{\mathrm{d}t} = \int \{E'D' + H'B' - \tfrac{1}{2}(E'\cdot D' + B'\cdot H')\mathsf{U}\}\cdot n\,\mathrm{d}S, \quad (371)$$

where (14) has been used. The right-hand side contains the field pressure tensor of Maxwell and Heaviside. The derivation shows that it corresponds to a material pressure which is the pressure $p_0(R_0)$ at a point R_0 in the liquid where the electromagnetic fields are zero. It will depend on the experimental situation whether such a pressure is accessible to measurement.

A second application of the expression (360) for the Kelvin pressure in an incompressible liquid consists in the evaluation of the radiation pressure on a metallic surface immersed in a liquid. Consider a plane electromagnetic wave

$$\begin{aligned} E_\mathrm{i} &= E_0 \cos{(\omega t - k\cdot R)}, \\ B_\mathrm{i} &= n(n \wedge E_0) \cos{(\omega t - k\cdot R)}, \end{aligned} \quad (372)$$

with ω the circular frequency, k the wave vector, n the refractive index and $n \equiv k/k$ the direction of propagation, hitting a plane metallic surface perpendicularly. The wave is assumed to be totally reflected, so that its reflected part has the form

$$\begin{aligned} E_\mathrm{r} &= -E_0 \cos{(\omega t + k\cdot R)}, \\ B_\mathrm{r} &= n(n \wedge E_0) \cos{(\omega t + k\cdot R)} \end{aligned} \quad (373)$$

(the metallic surface passes through the origin of coordinates). If one averages the law (150) or (109) over a period $2\pi\omega^{-1}$, one finds, taking the fluid to be at rest, that

$$\nabla\cdot\{\overline{\mathsf{P}} - \overline{DE} - \overline{BH} + (\tfrac{1}{2}\overline{E^2} + \tfrac{1}{2}\overline{B^2} - \overline{M\cdot B})\mathsf{U}\} = 0, \quad (374)$$

where the bars indicate time averages. Applying this formula to a cylinder with unit cross-section and its axis parallel to n, lying half in the fluid and half in the metal, one obtains upon using Gauss's theorem

$$n\cdot\overline{\mathsf{P}}_\mathrm{fluid} - n\cdot\overline{\mathsf{P}}_\mathrm{metal} + (\tfrac{1}{2}\overline{E^2} + \tfrac{1}{2}\overline{B^2} - \overline{M\cdot B})n = 0. \quad (375)$$

If the fluid is assumed to be in equilibrium, its time averaged pressure is diagonal and follows from (360). (The time derivative $c^{-1}(\partial/\partial t)(P \wedge B)$ which is present in (361) drops out if one employs it for time averaged quantities.) Then one finds:

$$n\cdot\overline{\mathsf{P}}_\mathrm{metal} = \bar{p}_\mathrm{fluid,0}(R_0)n + \tfrac{1}{2}\{\overline{D(R)\cdot E(R)} + \overline{B(R)\cdot H(R)}\}n, \quad (376)$$

where R is a position in the light beam and R_0 a position outside of it. The average values occurring in the second term at the right-hand side follow from (372–373). One gets $2\varepsilon E_0^2 n$, because the refractive index n is equal to $(\varepsilon\mu)^{\frac{1}{2}}$. Therefore one obtains as the radiation pressure, which is the difference of the left-hand side and the first term at the right-hand side of (376)

$$p_\mathrm{rad} = 2\varepsilon E_0^2. \quad (377)$$

Introducing the amplitude of the absolute value of the Poynting vector $S = cE \wedge H$ of the incident wave, which is

$$|S| = c\sqrt{\frac{\varepsilon}{\mu}}\,E_0^2, \quad (378)$$

one finds for the radiation pressure

$$p_\mathrm{rad} = 2c^{-1}n|S|. \quad (379)$$

For the case of vacuum ($n = 1$) this result has been found experimentally[1]. If one compares radiation pressures in different media, keeping $|S|$ constant, one finds from (379) that the radiation pressures are proportional to the refractive index, a second result which has been checked experimentally[2]. The derivation shows that due to the time averaging the terms with time derivatives in the momentum law drop out: in other words neither the material nor the field momentum density play a role in the discussion of radiation pressure.

b. Crystalline solids

Amorphous and polycrystalline solids may be discussed along similar lines as above. In contrast with these, crystalline solid systems cannot be described by thermodynamics in local formulation: only global laws could be derived in the preceding section. Yet it is possible, at least in principle, to find the

[1] P. Lebedew, Ann. Physik 6(1901)433; E. F. Nichols and G. F. Hull, Phys. Rev. 13(1901) 307, 17(1903)26.

[2] R. V. Jones, Nature 167(1951)439; R. V. Jones and J. C. S. Richards, Proc. Roy. Soc. 221A(1954)480.

deformation of a solid system from thermodynamical considerations. To that end one may start from the entropy law (294). The infinitesimal deformation tensor $\delta\boldsymbol{\epsilon}$ may be expressed in terms of state variables by means of relation (311). If the solid does not rotate, (i.e. if $\boldsymbol{\eta}_A = 1$) and if only small deformations are considered, one finds from (294) for the change of free energy $F^* \equiv U^* - TS$ for a solid at rest in a uniform external field:

$$dF^* = -S\,dT - \int^S \boldsymbol{n}\cdot\mathbf{P}(\boldsymbol{R})\cdot d\boldsymbol{\eta}(\boldsymbol{R})\cdot\boldsymbol{R}\,dS$$
$$- \tfrac{1}{2}\int^S \boldsymbol{n}\cdot d\boldsymbol{\eta}(\boldsymbol{R})\cdot\boldsymbol{R}\{\mathbf{P}(\boldsymbol{R})\cdot\boldsymbol{n}\}^2\,dS - V\overline{\mathbf{P}}\cdot d\boldsymbol{E}_e - V\overline{\mathbf{M}}\cdot d\boldsymbol{B}_e. \quad (380)$$

(In contrast to the preceding subsection no primes were added although again rest frame quantities are meant.) From this relation one may find the difference of the free energies in the presence (F^*) and absence (F_0^*) of external fields, at constant surface deformation $\boldsymbol{\eta}(\boldsymbol{R})$ and temperature T:

$$F^* - F_0^* = -V\int (\overline{\mathbf{P}}\cdot d\boldsymbol{E}_e + \overline{\mathbf{M}}\cdot d\boldsymbol{B}_e). \quad (381)$$

If in particular the polarizations are proportional to the fields one finds simply

$$F^* - F_0^* = -\tfrac{1}{2}V(\overline{\mathbf{P}}\cdot\boldsymbol{E}_e + \overline{\mathbf{M}}\cdot\boldsymbol{B}_e). \quad (382)$$

The relation (380) then shows that the difference of the pressure tensor at the surface (contracted with the normal on the surface) in the presence and in the absence of external fields follows by taking a functional derivative of (381) (or (382)) with respect to $\boldsymbol{\eta}(\boldsymbol{R})$, the deformation tensor at the surface. Since the (normal component of the) pressure tensor in the presence of external fields follows directly from the Liénard expression (241), we find in this way the normal pressure at the surface in the absence of external fields, but with the same values of the temperature and of the deformation tensor. Hence the problem to find the deformation $\boldsymbol{\eta}(\boldsymbol{R})$ at the surface under the influence of external fields has been reduced now to a problem of ordinary (field-free) elasticity theory.

The programme as sketched above is not feasible in general since the determination of the functional derivative of (381) presents difficulties in practical cases. One of these is the way in which the shape of the sample enters through the occurrence of the external fields instead of the Maxwell fields. A way to avoid this difficulty is to start from a second law which contains the Maxwell fields rather than the external fields, namely relation (321)

(valid for an ellipsoidal sample), which entails a free energy change

$$dF = -S\,dT - \int^S \boldsymbol{n}\cdot\mathbf{P}(\boldsymbol{R})\cdot d\boldsymbol{\eta}(\boldsymbol{R})\cdot\boldsymbol{R}\,dS + \boldsymbol{E}\cdot d(V\boldsymbol{P}) - V\boldsymbol{M}\cdot d\boldsymbol{B}. \quad (383)$$

Again we assumed that the solid does not rotate and that only small deformations occur. The sample has been chosen ellipsoidal, so that the polarizations and fields are approximately uniform. The difference $F - F_0$ of the free energy in the presence and the absence of external fields, but with the same surface deformation $\boldsymbol{\eta}(\boldsymbol{R})$ and temperature T may now be found. We assume that the polarizations depend on the Maxwell fields through linear relations of the form

$$\boldsymbol{P} = \boldsymbol{\varkappa}(\boldsymbol{\eta}, T)\cdot\boldsymbol{E},$$
$$\boldsymbol{M} = \boldsymbol{\chi}(\boldsymbol{\eta}, T)\cdot\boldsymbol{B}, \quad (384)$$

with symmetrical susceptibility tensors $\boldsymbol{\varkappa}$ and $\boldsymbol{\chi}$ (v. (322)). In these relations $\boldsymbol{\eta}$ stands for the whole set of deformation tensors everywhere at the surface. Therefore one may write for small deformations the following expressions

$$\boldsymbol{\varkappa}^{-1}(\boldsymbol{\eta}, T) = \boldsymbol{\varkappa}_0^{-1}(T) + \frac{1}{V}\int^S \boldsymbol{\varkappa}_1^{-1}(\boldsymbol{R}, T)\cdot\{\boldsymbol{\eta}(\boldsymbol{R}) - \mathbf{U}\}\cdot\boldsymbol{R}\,dS,$$
$$\boldsymbol{\chi}(\boldsymbol{\eta}, T) = \boldsymbol{\chi}_0(T) + \frac{1}{V}\int^S \boldsymbol{\chi}_1(\boldsymbol{R}, T)\cdot\{\boldsymbol{\eta}(\boldsymbol{R}) - \mathbf{U}\}\cdot\boldsymbol{R}\,dS, \quad (385)$$

for the inverse electric and the magnetic susceptibilities. ($\boldsymbol{\varkappa}_0^{-1}$ and $\boldsymbol{\chi}_0$ are tensors of the second rank, while $\boldsymbol{\varkappa}_1^{-1}$ and $\boldsymbol{\chi}_1$ have three indices.) From (383) with (384) it follows that one has

$$F - F_0 = \tfrac{1}{2}V(\boldsymbol{P}\cdot\boldsymbol{E} - \boldsymbol{M}\cdot\boldsymbol{B}). \quad (386)$$

By differentiating this relation functionally with respect to $\boldsymbol{\eta}(\boldsymbol{R})$ at constant temperature T, total electric polarization $V\boldsymbol{P}$ and magnetic field $\boldsymbol{B}$, one finds, according to (383), the normal component of the difference between the pressure tensors at the surface in the presence and in the absence of fields:

$$\boldsymbol{n}\cdot\{\mathbf{P}(\boldsymbol{R}) - \mathbf{P}_0(\boldsymbol{R})\} = -\tfrac{1}{2}\boldsymbol{PP} : \boldsymbol{\varkappa}_1^{-1}(\boldsymbol{R}, T) + \tfrac{1}{2}\boldsymbol{BB} : \boldsymbol{\chi}_1(\boldsymbol{R}, T) + \tfrac{1}{2}(\boldsymbol{P}\cdot\boldsymbol{E} + \boldsymbol{M}\cdot\boldsymbol{B})\boldsymbol{n}. \quad (387)$$

Here we used the fact that the volume change that accompanies an infinitesimal change of a deformation $\boldsymbol{\eta}$ is given by

$$dV = \int \boldsymbol{n}\cdot d\boldsymbol{\eta}(\boldsymbol{R})\cdot\boldsymbol{R}\,dS, \quad (388)$$

as follows from the definition of $\boldsymbol{\eta}$. (For a fluid it follows from the isotropy of the system and the fact that the susceptibilities depend only on the total volume of the system, that

$$\boldsymbol{\varkappa}_0^{-1}(T) = \mathbf{U}\kappa^{-1}(T),$$

$$\boldsymbol{\varkappa}_1^{-1}(T) = \mathbf{U}nv\,\frac{\partial\kappa^{-1}(v, T)}{\partial v} \tag{389}$$

and similarly for the magnetic susceptibilities[1]. Indeed one finds back now (344) from (387).)

With the help of the Liénard expression (241) we obtain now for the normal component of the pressure tensor in the absence of fields, but with the same deformation at the surface and the same temperature:

$$\boldsymbol{n}\cdot\mathbf{P}_0(\boldsymbol{R}) = \boldsymbol{n}\cdot\mathbf{P}_{\text{out}}(\boldsymbol{R}) - \tfrac{1}{2}n(\boldsymbol{P}\cdot\boldsymbol{n})^2 + \tfrac{1}{2}\boldsymbol{P}\boldsymbol{P} : \boldsymbol{\varkappa}_1^{-1}(\boldsymbol{R},\, T)$$

$$- \tfrac{1}{2}\boldsymbol{B}\boldsymbol{B} : \boldsymbol{\chi}_1(\boldsymbol{R},\, T) - \tfrac{1}{2}(\boldsymbol{P}\cdot\boldsymbol{E} + \boldsymbol{M}\cdot\boldsymbol{B})\boldsymbol{n}, \tag{390}$$

with $\mathbf{P}_{\text{out}}$ the pressure outside the system (in the presence of fields). The expression (390) may be looked upon as a boundary condition for an ordinary (field-free) elasticity problem. It shows that the boundary value $\boldsymbol{n}\cdot\mathbf{P}_0$ consists of two parts, 1st: two terms that represent the effect of the outward and Liénard pressures (the corresponding deformation is called the electrostrictive form effect), and 2nd: three terms which contain the constants that characterize the material and which form a generalization to solids of (minus) the right-hand side of (344) (the corresponding deformation is called the electro- and magnetostriction effect *sensu stricto*).

For a uniform scalar outward pressure – as the atmospheric pressure – one may evaluate, with the usual methods of elasticity, the deformation at the surface of the sample due to the form effect, at least for spherical shapes cut from substances with simple crystal symmetries (as for instance the cubic symmetries)[2]. One finds in this way a non-uniform deformation at the surface. Comparison with the experimental data showed that the total deformation at the surface has the same non-uniform character in the sense that there is a uniform difference. This means that the proper electro-magnetostriction gives rise to a uniform deformation over the surface. One may

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[1] Note that the specific volume v enters as a parameter at the right-hand side. This corresponds to the parametric dependence in (384) of the quantities κ and χ on the reference state with respect to which $\boldsymbol{\eta}$ is defined.

[2] R. Gersdorf, Physica **26**(1960)553 for the magnetostrictive case; v. also R. R. Birss and S. R. Adamson, Brit. J. Appl. Phys. **1**(1968)631, R. R. Birss and B. C. Hegarty, Brit. J. Appl. Phys. **1**(1968)789 for the calculation of the form effect for prolate spheroids.

conclude from this fact that the tensors $\boldsymbol{\varkappa}_1^{-1}$ and $\boldsymbol{\chi}_1$, which occur in (390), have the following dependence on the position $\boldsymbol{R}$

$$\{\boldsymbol{\varkappa}_1^{-1}(\boldsymbol{R},\, T)\}^{ijk} = n_l\{\hat{\boldsymbol{\varkappa}}_1^{-1}(T)\}^{ijlk},$$

$$\{\boldsymbol{\chi}_1(\boldsymbol{R},\, T)\}^{ijk} = n_l\{\hat{\boldsymbol{\chi}}_1(T)\}^{ijlk}, \tag{391}$$

where the fourth-rank symbols (symmetric in i and j) are independent of the position at the surface, the only dependence on $\boldsymbol{R}$ being represented by the outward normal unit vector $\boldsymbol{n}$ (which occurs also in the left-hand side of (390)). The theory of the proper electro-magnetostriction is concerned now with the study of the quantities $\hat{\boldsymbol{\varkappa}}_1^{-1}(T)$ and $\hat{\boldsymbol{\chi}}_1(T)$. (A microscopic theory of electro-magnetostriction will be given for a simple model of a magnetic material in chapter X, § 6.) Phenomenologically one may employ the crystal symmetry to reduce the number of independent electro-magnetostriction constants, which occur in the two tensors of the fourth rank in (391). For instance for an isotropic or polycrystalline solid the number of independent electrostriction components $\hat{\boldsymbol{\varkappa}}_1^{-1}(T)$ reduces from 54 to 2 since one has then

$$(\hat{\boldsymbol{\varkappa}}_1^{-1})^{ijkl} = a\delta^{ij}\delta^{kl} + b(\delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk}), \tag{392}$$

because the Kronecker deltas are the only invariant quantities with respect to rotations. (For fluid systems it follows from (389) that b vanishes while a is equal to $v\partial\kappa^{-1}/\partial v$.) Similar remarks apply to the magnetostriction constants.

APPENDIX I

On the depolarizing tensor

In section 7b occurs the integral (219), which in general depends on the position R. We want to prove first that for an ellipsoidal volume the integral is in fact independent of R (if R is inside the volume) so that we then have

$$\int^V \nabla'\nabla' \frac{1}{4\pi|R-R'|}\,dR' = \int^V \nabla'\nabla' \frac{1}{4\pi|R'|}\,dR' \equiv -\mathbf{L},\qquad (A1)$$

where the centre of the ellipsoid has been chosen as the origin of the coordinate system. The quantity $\mathbf{L}$ is called the 'depolarizing tensor'.

The second integral in (A1) depends only on the shape of the ellipsoidal volume and not on its scale, so that we may replace it by an integral over a small volume around the origin and of the same shape as the ellipsoid. This means that it is sufficient to prove instead of (A1) the vanishing of the integral

$$\mathscr{P}\int^V \nabla'\nabla' \frac{1}{4\pi|R-R'|}\,dR',\qquad (A2)$$

where the principal value sign indicates that an infinitesimal ellipsoid of the same shape as the large one with centre R has to be excluded from the integration over R'. By a conveniently chosen linear transformation of coordinates

$$\hat{R} = \mathbf{A}\cdot R,\qquad (A3)$$

it is possible to transform the ellipsoid to a sphere. Then it becomes sufficient to prove the vanishing of the integral (omitting the circumflexes of $\hat{R}$ and $\hat{R}'$):

$$\mathscr{P}_0\int^{V_0} \nabla'\cdot\mathbf{A}\nabla'\cdot\mathbf{A} \frac{1}{4\pi|\mathbf{A}^{-1}\cdot(R-R')|}(\det\mathbf{A})^{-1}dR',\qquad (A4)$$

where the integration is now extended over a spherical volume V_0 and where the principal value sign indicates the exclusion of an infinitesimal sphere around R from the integration over R'. The denominator may be written as $4\pi|(R-R')+(\mathbf{A}^{-1}-\mathbf{U})\cdot(R-R')|$. Then, if the reciprocal of this expression

is Taylor expanded, it follows that it is sufficient to prove that for all integer $n \geqslant 0$ the integral

$$\mathscr{P}_0\int^{V_0} \nabla'\nabla'(R-R')^n\nabla'^n \frac{1}{4\pi|R-R'|}\,dR'\qquad (A5)$$

vanishes.

Let us first consider these integrals for $R = 0$. With Gauss's theorem, (A5) becomes for this case, apart from a factor $(-1)^n$,

$$\int^{S_0} n'\nabla'R'^n\nabla'^n \frac{1}{4\pi|R'|}\,dS' - \int^{s_0} n'\nabla'R'^n\nabla'^n \frac{1}{4\pi|R'|}\,dS',\qquad (A6)$$

where S_0 is the surface of the large sphere, and s_0 of the infinitesimal one; n' is the unit vector normal to the integration surfaces. Each of the integrals is independent of the scale of the sphere so that they are equal. Hence the expression (A6) vanishes.

Since now the vanishing of (A5) is proved for the case $R = 0$, it is sufficient to prove that (A5) is independent of R in order to ensure its vanishing everywhere. The derivative of (A5) with respect to R is

$$-\int^{S_0} n'\nabla'\nabla'(R-R')^n\nabla'^n \frac{1}{4\pi|R-R'|}\,dS'.\qquad (A7)$$

To prove the vanishing of this derivative we expand the integrand with respect to R. We find then that it is sufficient to prove the vanishing of the expression

$$\int^{S_0} n'\nabla'^{m+2}\left(R'^n\nabla'^n \frac{1}{4\pi|R'|}\right)dS'\qquad (A8)$$

for all $m, n \geqslant 0$, or alternatively the vanishing of

$$\int^{S_0} n'R'^n\nabla'^{n+m+2} \frac{1}{4\pi|R'|}\,dS'.\qquad (A9)$$

This integral is an *invariant* tensor of rank $2n+m+3$, which is symmetric in the second up to and including the $(n+1)$th Cartesian index, and symmetric in the last $n+m+2$ indices. Moreover the traces taken with a pair of indices from the last $n+m+2$ vanish, since $\Delta'(1/4\pi|R'|)$ is zero for $R' \neq 0$. Therefore (A9) is an element of the direct product space of tensors of rank 1, symmetric tensors of rank n and symmetric, traceless tensors of rank $n+m+2$. Symmetric tensors of rank n form a reducible representation of the rotation group which contains irreducible representations of dimension $2n+1$ and lower, whereas symmetric, traceless tensors of rank $n+m+2$

form an irreducible representation of dimension $2n+2m+5$. The direct product of tensors of these two types contains only irreducible representations of a dimensionality $2m+5$ and higher, so that the direct product space mentioned above, of which (A9) is an element, contains irreducible representations of dimensionality higher than 1. Since (A9) is an *invariant* tensor in this direct product space it must vanish identically. Thus, retracing the chain of reasoning, it is now proved that the first member of (A1) is indeed independent of R, and hence equal to minus the depolarizing tensor $\mathbf{L}$.

As a corollary of (A1) one finds by integrating over R:

$$\iint^{V} \mathbf{V}'\mathbf{V}' \frac{1}{4\pi|R-R'|} \, dR \, dR' = -V\mathbf{L}, \tag{A10}$$

a formula which has been used in (231).

In a way analogous to the proof given above one may show that the integral

$$\int^{V} (R-R')\mathbf{V}'\mathbf{V}'\mathbf{V}' \frac{1}{8\pi|R-R'|} \, dR' \tag{A11}$$

is independent of R, so that we may write

$$\int^{V} (R-R')\mathbf{V}'\mathbf{V}'\mathbf{V}' \frac{1}{8\pi|R-R'|} \, dR' = \int^{V} (R-R')\mathbf{V}'\mathbf{V}'\mathbf{V}' \frac{1}{8\pi|R'|} \, dR' \equiv -\tfrac{1}{2}\mathbf{K},$$

$$\tag{A12}$$

where $\mathbf{K}$ is a tensor with four Cartesian indices. As a corollary it follows that

$$\iint^{V} (R-R')\mathbf{V}'\mathbf{V}'\mathbf{V}' \frac{1}{8\pi|R-R'|} \, dR \, dR' = -\tfrac{1}{2}V\mathbf{K}. \tag{A13}$$

Finally we want to prove the identity

$$\delta\mathbf{L} = (\mathrm{Tr}\ \delta\boldsymbol{\epsilon})\mathbf{L} - \delta\boldsymbol{\epsilon} : \mathbf{K}, \tag{A14}$$

which gives the variation of the tensor $\mathbf{L}$ when the boundary of the ellipsoidal volume is deformed according to

$$\delta R = \delta\boldsymbol{\epsilon}\cdot R, \tag{A15}$$

where $\delta\boldsymbol{\epsilon}$ is the (uniform) deformation tensor and where the centre of the ellipsoid is the origin of the coordinate system. From the definition (A1) of $\mathbf{L}$ one has

$$\delta\mathbf{L} = -\int^{S} \mathbf{n}\cdot\delta R\mathbf{V}\mathbf{V} \frac{1}{4\pi|R|} \, dS, \tag{A16}$$

where the integration is extended over the surface of the ellipsoid with normal $\mathbf{n}$. With Gauss's theorem and (A15) this becomes

$$\delta\mathbf{L} = -\int^{V} \mathbf{V}\cdot \left(\delta\boldsymbol{\epsilon}\cdot R\mathbf{V}\mathbf{V} \frac{1}{4\pi|R|}\right) \, dR. \tag{A17}$$

Performing the differentiation one gets

$$\delta\mathbf{L} = -(\mathrm{Tr}\ \delta\boldsymbol{\epsilon})\int^{V} \mathbf{V}\mathbf{V} \frac{1}{4\pi|R|} \, dR - \int^{V} \delta\boldsymbol{\epsilon} : R\mathbf{V}\mathbf{V}\mathbf{V} \frac{1}{4\pi|R|} \, dR, \tag{A18}$$

which in view of the definitions of $\mathbf{L}$ and $\mathbf{K}$ is indeed (A14).

A corollary is obtained by noting that $\mathrm{Tr}\ \delta\boldsymbol{\epsilon}$ is $V^{-1}\delta V$ with V the volume of the ellipsoid:

$$\delta(V^{-1}\mathbf{L}) = -V^{-1}\delta\boldsymbol{\epsilon} : \mathbf{K}. \tag{A19}$$

It has been employed in subsection 7b (246).

As an example let us derive the tensors $\mathbf{L}$ and $\mathbf{K}$ for a sphere. From (A1) it follows for a sphere that $\mathbf{L}$ is an invariant tensor with two indices and hence a multiple of the unit tensor. The factor is determined by calculating the trace of $\mathbf{L}$:

$$\mathrm{Tr}\ \mathbf{L} = -\int^{V} \varDelta \frac{1}{4\pi|R|} \, dR = 1, \tag{A20}$$

so that for the sphere

$$\mathbf{L} = \tfrac{1}{3}\mathbf{U}. \tag{A21}$$

Furthermore it follows from (A12) for a sphere that $\mathbf{K}$ is an invariant tensor with four indices and hence of the form

$$K_{ijkl} = \alpha\delta_{ij}\delta_{kl} + \beta\delta_{ik}\delta_{jl} + \gamma\delta_{il}\delta_{jk}. \tag{A22}$$

From the symmetry of $\mathbf{K}$ in its last three indices (see the definition (A12)) it follows that α, β and γ are equal. Furthermore through contraction of the last pair of indices one has:

$$\mathbf{K} : \mathbf{U} = -\int R\mathbf{V}\delta(R)dR = \mathbf{U} \tag{A23}$$

as follows from partial integration. In this way we have obtained for a sphere:

$$K_{ijkl} = \tfrac{1}{5}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \tag{A24}$$

The identity (A14) becomes for small deformations of the sphere

$$\delta\mathbf{L} = \tfrac{2}{15}(\mathrm{Tr}\ \delta\boldsymbol{\epsilon})\mathbf{U} - \tfrac{1}{5}\delta\boldsymbol{\epsilon} - \tfrac{1}{5}\delta\tilde{\boldsymbol{\epsilon}}, \tag{A25}$$

where the results (A21) and (A24) have been utilized.

<div style="text-align:center">

APPENDIX II

The Hamiltonian for a system of composite particles in an external field

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The Hamiltonian of a system of particles ki (grouped in atoms or other stable entities numbered by k, while the constituent particles are labelled by $i = 1, 2, \ldots, f$) with charges e_{ki}, positions R_{ki} and momenta P_{ki}, which move in an external field with scalar and vector potentials φ_e and A_e, reads up to order c^{-1} (v. (I.16)):

$$H(R_{ki}, P_{ki}, t) = \sum_{k,i} \frac{P_{ki}^2}{2m_{ki}} + \sum_k \sum_{i,j(i \neq j)} \frac{e_{ki} e_{kj}}{8\pi |R_{ki} - R_{kj}|}$$
$$+ \sum_{k,l(k \neq l)} \sum_{i,j} \frac{e_{ki} e_{lj}}{8\pi |R_{ki} - R_{lj}|} + \sum_{k,i} e_{ki} \left\{ \varphi_e(R_{ki}, t) - c^{-1} \frac{P_{ki}}{m_{ki}} \cdot A_e(R_{ki}, t) \right\}. \quad \text{(A26)}$$

Let us now introduce new canonical coordinates q_{ki} and momenta $\hat{p}_{ki}$, such that the q_{ki} are the centre of mass of atom k and (independent) relative coordinates of the constituent particles with respect to this centre:

$$q_{ki} = R_{ki} - R_k \equiv R_{ki} - \sum_{j=1}^{f} (m_{kj}/m_k) R_{kj}, \quad (i = 1, \ldots, f-1),$$

$$q_{kf} = R_k \equiv \sum_{j=1}^{f} (m_{kj}/m_k) R_{kj},$$

$$\hat{p}_{ki} = P_{ki} - (m_{ki}/m_{kf}) P_{kf}, \quad (i = 1, \ldots, f-1),$$

$$\hat{p}_{kf} = \sum_{i=1}^{f} P_{ki}. \quad \text{(A27)}$$

This is a canonical transformation, as may be checked by evaluating the Poisson brackets. Inversion of (A27) gives

$$R_{ki} = q_{kf} + (1 - \delta_{if}) q_{ki} - \delta_{if} \sum_{j=1}^{f-1} (m_{kj}/m_{kf}) q_{kj},$$

$$P_{ki} = (m_{ki}/m_k) \hat{p}_{kf} + (1 - \delta_{if}) \hat{p}_{ki} - (m_{ki}/m_k) \sum_{j=1}^{f-1} \hat{p}_{kj}. \quad \text{(A28)}$$

We substitute these relations into the Hamiltonian (A26) and expand the

potentials around the centres of mass R_k, retaining only terms up to first derivatives of the potentials:

$$H(q, \hat{p}, t) = \sum_k \left(\frac{\hat{p}_{kf}^2}{2m_k} + \sum_{i=1}^{f-1} \frac{\hat{p}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{\hat{p}_{ki} \cdot \hat{p}_{kj}}{2m_k} \right)$$
$$+ \sum_k \sum_{i,j=1(i \neq j)}^{f} \frac{e_{ki} e_{kj}}{8\pi |R_{ki}(q) - R_{kj}(q)|} + \sum_{k,l(k \neq l)} \sum_{i,j=1}^{f} \frac{e_{ki} e_{lj}}{8\pi |R_{ki}(q) - R_{lj}(q)|}$$
$$+ \sum_k e_k \left\{ \varphi_e(R_k, t) - c^{-1} \frac{\hat{p}_{kf}}{m_k} \cdot A_e(R_k, t) \right\}$$
$$+ \sum_k \sum_{i=1}^{f} e_{ki} \left[\{R_{ki}(q) - q_{kf}\} \cdot \nabla_k \left\{ \varphi_e(R_k, t) - c^{-1} \frac{\hat{p}_{kf}}{m_k} \cdot A_e(R_k, t) \right\} \right.$$
$$- c^{-1} \left\{ \frac{P_{ki}(\hat{p})}{m_{ki}} - \frac{\hat{p}_{kf}}{m_k} \right\} \cdot A_e(R_k, t)$$
$$\left. - c^{-1} \{R_{ki}(q) - q_{kf}\} \cdot \nabla_k A_e(R_k, t) \cdot \left\{ \frac{P_{ki}(\hat{p})}{m_{ki}} - \frac{\hat{p}_{kf}}{m_k} \right\} \right], \quad \text{(A29)}$$

where $R_{ki}(q)$ and $P_{ki}(\hat{p})$ stand for the right-hand sides of (A28). This expression may be transformed by means of a second canonical transformation in order to cast the last three terms in gauge invariant form. This transformation is given by the generating function:

$$F(q, p, t) = \sum_k R_k \cdot P_k + \sum_k \sum_{i=1}^{f-1} q_{ki} \cdot p_{ki}$$
$$+ c^{-1} \sum_k \sum_{i=1}^{f} e_{ki} A_e(R_k, t) \cdot \{R_{ki}(q) - q_{kf}\}$$
$$+ \tfrac{1}{2} c^{-1} \sum_k \sum_{i=1}^{f} e_{ki} \{R_{ki}(q) - q_{kf}\} \cdot \nabla_k A_e(R_k, t) \cdot \{R_{ki}(q) - q_{kf}\}, \quad \text{(A30)}$$

depending on the old coordinates q_{ki}, $q_{kf} \equiv R_k$, the new momenta p_{ki}, $p_{kf} \equiv P_k$ and time. With the help of the transformation formulae

$$q_{ki} = \frac{\partial F}{\partial p_{ki}} \quad (i = 1, \ldots, f-1), \qquad R_k = \frac{\partial F}{\partial P_k},$$
$$\hat{p}_{ki} = \frac{\partial F}{\partial q_{ki}} \quad (i = 1, \ldots, f-1), \qquad \hat{p}_{kf} = \frac{\partial F}{\partial R_k}, \quad \text{(A31)}$$

it follows that the coordinates do not change. Furthermore the new Hamiltonian gets an extra term $\partial F/\partial t$. If we substitute (A31) with (A30) into (A29), neglecting again second derivatives of the potentials, and using the vector

identity $(a \wedge b) \cdot (c \wedge d) = (a \cdot c)(b \cdot d) - (a \cdot d)(b \cdot c)$, we get as the new Hamiltonian (up to c^{-1}):

$$H(q, p, t) = \sum_k \left(\frac{P_k^2}{2m_k} + \sum_{i=1}^{f-1} \frac{p_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{p_{ki} \cdot p_{kj}}{2m_k} \right)$$

$$+ \sum_k \sum_{i,j=1(i \neq j)}^{f} \frac{e_{ki} e_{kj}}{8\pi |R_{ki}(q) - R_{kj}(q)|} + \sum_{k,l(k \neq l)} \sum_{i,j=1}^{f} \frac{e_{ki} e_{lj}}{8\pi |R_{ki}(q) - R_{lj}(q)|}$$

$$+ \sum_k e_k \left\{ \varphi_e(R_k, t) - c^{-1} \frac{P_k}{m_k} \cdot A_e(R_k, t) \right\}$$

$$- \sum_k \left\{ \bar{\mu}_k^{(1)} \cdot E_e(R_k, t) + \left(\bar{v}_k^{(1)} + c^{-1} \bar{\mu}_k^{(1)} \wedge \frac{P_k}{m_k} \right) \cdot B_e(R_k, t) \right\}, \tag{A32}$$

with the abbreviations

$$\bar{\mu}_k^{(1)}(q) \equiv \sum_{i=1}^{f} e_{ki} \{ R_{ki}(q) - q_{kf} \},$$

$$\bar{v}_k^{(1)}(q, p) \equiv \tfrac{1}{2} c^{-1} \sum_{i=1}^{f} e_{ki} \{ R_{ki}(q) - q_{kf} \} \wedge \left\{ (1 - \delta_{if}) \frac{p_{ki}}{m_{ki}} - \sum_{j=1}^{f-1} \frac{p_{kj}}{m_k} \right\}. \tag{A33}$$

These quantities are the electric and magnetic dipole moments, written in terms of the canonical coordinates and momenta. For the electric dipole moment this is obvious since $q_{kf} \equiv R_k$, the position of the centre of mass. For the magnetic dipole moment it follows because the Hamilton equations yield up to c^0:

$$(1 - \delta_{if}) \frac{p_{ki}}{m_{ki}} - \sum_{j=1}^{f-1} \frac{p_{kj}}{m_k} = \dot{R}_{ki}(q) - \dot{q}_{kf}. \tag{A34}$$

(We note in passing that the Hamiltonian equations for the coordinates R_k and momenta P_k lead indeed to the equations of motion (I.50).)

We shall need also an expression for the kinetic energy of the system:

$$K(q, \dot{q}, t) \ \left(\equiv \sum_k \sum_{i=1}^{f} \tfrac{1}{2} m_{ki} \dot{R}_{ki}^2 \right)$$

$$= \sum_k \tfrac{1}{2} m_k \dot{R}_k^2 + \sum_k \left(\sum_{i=1}^{f-1} \tfrac{1}{2} m_{ki} \dot{q}_{ki}^2 + \sum_{i,j=1}^{f-1} \frac{m_{ki} m_{kj}}{2m_{kf}} \dot{q}_{ki} \cdot \dot{q}_{kj} \right), \tag{A35}$$

where (A28) has been used. We may express it in terms of the coordinates and momenta, by using the Hamilton equations $\dot{q}_{ki} = \partial H / \partial p_{ki}$ with (A32–

33). Then we get up to c^{-1}

$$K(q, p, t) = \sum_k \left\{ \frac{P_k^2}{2m_k} - c^{-1} e_k \frac{P_k}{m_k} \cdot A_e(R_k, t) - c^{-1} \left(\bar{\mu}_k^{(1)} \wedge \frac{P_k}{m_k} \right) \cdot B_e(R_k, t) \right\}$$

$$+ \sum_k \left\{ \sum_{i=1}^{f-1} \frac{p_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{p_{ki} \cdot p_{kj}}{2m_k} - \bar{v}_k^{(1)} \cdot B_e(R_k, t) \right\}. \tag{A36}$$

Therefore the Hamiltonian (A32) may be written in the form

$$H(q, p, t) = K(q, p, t) + \sum_k \sum_{i,j=1(i \neq j)}^{f} \frac{e_{ki} e_{kj}}{8\pi |R_{ki}(q) - R_{kj}(q)|}$$

$$+ \sum_{k,l(k \neq l)} \sum_{i,j=1}^{f} \frac{e_{ki} e_{lj}}{8\pi |R_{ki}(q) - R_{lj}(q)|} + \sum_k e_k \varphi_e(R_k, t) - \sum_k \bar{\mu}_k^{(1)} \cdot E_e(R_k, t). \tag{A37}$$

It should be noted that the terms with the vector potential and the magnetic field appear explicitly in (A32) but are hidden in the kinetic energy in (A37).

APPENDIX III

Deformations and free energy

In this appendix we want to study the change of the free energy F^* with the change of the boundaries of the system.

The system considered consists of atoms, carrying charges and dipole moments, in a uniform and time-independent external field E_e, B_e. It is then described by the Hamiltonian (A32) of appendix II. At equilibrium it is represented by the canonical ensemble:

$$e^{-F^*/kT} = C \int^V e^{-H/kT} dq \, dp, \qquad (A38)$$

where V is the volume and T the temperature. (The constant C depends only on the particle number.) The free energy is thus a function of T, E_e, B_e and the boundary of the volume V. The integrations over the coordinates q may be extended to infinity if a wall potential (which is infinite if one of the particles of the system is outside the volume V) is included in the Hamiltonian. We take as the wall potential

$$U^W = \sum_k U_k^W(R_k) \qquad (A39)$$

with the functions U_k^W zero for R_k inside the volume and infinite for R_k outside the volume. Here R_k is the centre of mass of the atom k. In the first instance one might be inclined to write as the wall potential $\sum_{k,i} U_{ki}^W(R_{ki})$, where the sum is extended over all constituent particles. However, since the dimensions of the stable atoms are small compared to the volume the use of (A39) instead of this expression is justified if surface effects are neglected. Thus we write instead of (A38)

$$e^{-F^*/kT} = C \int^\infty e^{-(H+U^W)/kT} dq \, dp. \qquad (A40)$$

Let us change the positions R^W of the walls by means of an infinitesimal transformation

$$R^{W'} = R^W + \delta R^W = \{U + \delta\epsilon(R^W)\} \cdot R^W \qquad (A41)$$

with an infinitesimal tensor $\delta\epsilon$ that depends on the position of the wall R^W. (The unit tensor is denoted by U.) Then the wall potential U^W is transformed to $U^{W'} = \sum_k U_k^{W'}(R_k)$, such that $U_k^{W'}$ is infinite if the position R_k is outside the new boundary, and zero inside. Alternatively one may say that $U_k^{W'}$ is infinite if $\{U - \delta\epsilon(R_k)\} \cdot R_k$ is outside the old boundary; in other words

$$U^{W'} = \sum_k U_k^W[\{U - \delta\epsilon(R_k)\} \cdot R_k]. \qquad (A42)$$

From (A40) we find now the change $\delta_\epsilon F^*$ of F^* with $\delta\epsilon$ at constant T, E_e and B_e:

$$\delta_\epsilon F^* = C\, e^{F^*/kT} \int^\infty \delta U^W e^{-(H+U^W)/kT} dq \, dp, \qquad (A43)$$

where $\delta U^W \equiv U^{W'} - U^W$. With (A42) this becomes, up to terms linear in $\delta\epsilon(R_k)$

$$\delta_\epsilon F^* = -\left\langle \sum_k R_k \cdot \delta\tilde{\epsilon}(R_k) \cdot \nabla_k U_k^W(R_k) \right\rangle, \qquad (A44)$$

where the brackets denote the canonical ensemble average and where $\delta\tilde{\epsilon}$ is the transposed matrix of $\delta\epsilon$. The right-hand side contains the force $-\nabla_k U_k^W(R_k)$ exerted by the wall on atom k. This expression is only different from zero if R_k is situated at the wall so that one may write it as a sum of contributions due to the various surface elements dS of the wall:

$$-\nabla_k U_k^W(R_k) = \int^S f_k^W(R_k)\delta(R_k - R)dS. \qquad (A45)$$

Inserting this expression into (A44), one finds

$$\delta_\epsilon F^* = \int^S R \cdot \delta\tilde{\epsilon}(R) \cdot f^W(R)dS, \qquad (A46)$$

where

$$f^W(R) \equiv \left\langle \sum_k f_k^W \delta(R_k - R) \right\rangle \qquad (A47)$$

is the average force per unit surface exerted by the wall. The latter is conventionally written as $-n \cdot P_{out}(R)$, where n is the outward normal to the boundary and $P_{out}(R)$ the pressure tensor in the wall. Therefore (A46) has the form

$$\delta_\epsilon F^* = -\int^S n \cdot P_{out} \cdot \delta\epsilon \cdot R \, dS. \qquad (A48)$$

An alternative expression for $\delta_\epsilon F^*$ is obtained if one uses the virial theo-

rem in the form

$$\left\langle \frac{d}{dt} \left\{ \sum_k P_k \cdot \delta\epsilon(R_k) \cdot R_k \right\} \right\rangle = 0, \tag{A49}$$

which follows from the fact that for a stationary ensemble the average of a total time derivative of a dynamical quantity vanishes. In (A49) the total time derivative has to be read as the Poisson bracket with the total Hamiltonian $H + U^W$, which includes the wall potential. Hence (A49) may be written as

$$\left\langle \sum_k \left\{ \frac{\partial U^W}{\partial R_k} \cdot \delta\epsilon(R_k) \cdot R_k + \frac{\partial H}{\partial R_k} \cdot \delta\epsilon(R_k) \cdot R_k - P_k \cdot \delta e(R_k) \cdot \frac{\partial H}{\partial P_k} \right\} \right\rangle = 0, \tag{A50}$$

where we introduced the infinitesimal deformation gradient tensor δe which is defined by a relation involving the partial derivatives of $\delta\epsilon$:

$$\delta\tilde{e}(R) \equiv \frac{\partial}{\partial R} \{\delta\epsilon(R) \cdot R\}. \tag{A51}$$

In particular if $\delta\epsilon$ represents a homogeneous deformation, i.e. is independent of R, we have

$$\delta e = \delta\epsilon. \tag{A52}$$

With the help of the identity (A50), we find for (A44)

$$\delta_\epsilon F^* = - \left\langle \sum_k \left\{ P_k \cdot \delta e(R_k) \cdot \frac{\partial H}{\partial P_k} - \frac{\partial H}{\partial R_k} \cdot \delta\epsilon(R_k) \cdot R_k \right\} \right\rangle. \tag{A53}$$

In particular if $\delta\epsilon$ is independent of the position, one finds for the change of the free energy

$$\delta_\epsilon F^* = A : \delta\epsilon \tag{A54}$$

with the tensor A defined as

$$A \equiv - \left\langle \sum_k \left(\frac{\partial H}{\partial P_k} P_k - R_k \frac{\partial H}{\partial R_k} \right) \right\rangle. \tag{A55}$$

The results (A53) and (A54–55) are used in the main text.

PROBLEMS

1.   Show that the solution of the first Maxwell equation $\nabla \cdot E = \varrho^e - \nabla \cdot P$ for the electrostatic case has the form given in the first line of (17). Check this by noting that one may replace the integral in the solution mentioned by one in which a small volume around R is excluded from the integration over R':

$$-\mathscr{P} \int \{\varrho^e(R', t) - \nabla' \cdot P(R', t)\} \nabla \frac{1}{4\pi|R-R'|} \, dR',$$

since the integral is convergent. The advantage of the latter way of writing the integral becomes apparent if one takes the divergence: the divergence of the integrand does not give a contribution now.

If in the expression given above a partial integration is performed in the second term, one finds for the electrostatic field an expression with convergent integrals:

$$E(R, t) = E_e(R, t) - \mathscr{P} \int \{\varrho^e(R', t) + P(R', t) \cdot \nabla'\} \nabla \frac{1}{4\pi|R-R'|} \, dR'$$
$$- \int^{s'} n' \cdot P(R', t) \nabla \frac{1}{4\pi|R-R'|} \, dS',$$

where s' is the surface of the small volume that is excluded from the integration in the first integral, while n' is the normal pointing in the direction away from R. The latter expression for $E(R, t)$ is conventionally written in the form of the first line of (71), which contains a semi-convergent integral.

An alternative form for the electric field may be obtained by starting again from (17), leaving the nabla operator outside the integral and performing a partial integration. Check that one obtains then

$$E(R, t) = E_e(R, t) - \nabla \int \{\varrho^e(R', t) + P(R', t) \cdot \nabla'\} \frac{1}{4\pi|R-R'|} \, dR',$$

which contains again convergent integrals. Going still one step further one may write all nabla operators before the integral

$$E(R, t) = E_e(R, t)$$
$$- \nabla \int \varrho^e(R', t) \frac{1}{4\pi|R-R'|} \, dR' + \nabla\nabla \cdot \int P(R', t) \frac{1}{4\pi|R-R'|} \, dR'$$

(with convergent integrals).

The second expression of this problem may also be obtained directly from the last formula.

2. Show by choosing for the excluded volume a small sphere with centre R, that one may write the electric field as

$$E(R, t) = E_e(R, t) - \mathscr{P}_{\text{sph}} \int \{\varrho^e(R', t) + P(R', t) \cdot \nabla'\} \nabla \frac{1}{4\pi|R-R'|} dR' - \tfrac{1}{3} P(R, t).$$

(The combination $E + \tfrac{1}{3}P$ is called the Lorentz cavity field.) Comparing this result with (71) one may write symbolically

$$\nabla_s \nabla_s \frac{1}{4\pi s} = \mathscr{P}_{\text{sph}} \nabla_s \nabla_s \frac{1}{4\pi s} - \tfrac{1}{3} U\delta(s)$$

with U the unit three-tensor. Taking the trace one finds

$$\varDelta_s \frac{1}{4\pi s} = -\delta(s).$$

Prove along similar lines the symbolic relation

$$s^i \nabla_s^j \nabla_s^k \nabla_s^l \frac{1}{4\pi s} = \mathscr{P}_{\text{sph}} s^i \nabla_s^j \nabla_s^k \nabla_s^l \frac{1}{4\pi s} + \tfrac{1}{5}(\delta^{ij}\delta^{kl} + \delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk})\delta(s)$$

(cf. (A24)). Contracting the indices i and j, one finds

$$s \cdot \nabla_s \nabla_s \nabla_s \frac{1}{4\pi s} = \mathscr{P}_{\text{sph}} s \cdot \nabla_s \nabla_s \nabla_s \frac{1}{4\pi s} + U\delta(s).$$

Comparing with the second relation of this problem, one obtains the identity

$$s \cdot \nabla_s \nabla_s \nabla_s \frac{1}{4\pi s} = -3 \nabla_s \nabla_s \frac{1}{4\pi s}.$$

(The identity is trivial for $s \neq 0$, since then it follows immediately by differentiation.)

3. Show by employing the equation of motion (found in problem 2 of chapter I) for a particle with dipoles and quadrupoles that the equation of motion for a fluid of neutral atoms with dipoles and quadrupoles has the

form (105) with the force density

$$F = (\nabla E) \cdot P + (\nabla B) \cdot M + c^{-1} \frac{\partial}{\partial t}(P \wedge B) + c^{-1} \nabla \cdot (vP \wedge B) + \varDelta F,$$

where P and M are the complete polarizations (39), including dipoles and quadrupoles. Furthermore the components of $\varDelta F$ read

$$\varDelta F^i = \nabla_j \left\{ (\nabla^i E_k) \bar{\mathscr{P}}^{(2)jk} + (\nabla^i B_k)(\bar{\mathscr{M}}^{(2)jk} + c^{-1} \varepsilon^{klm} \bar{\mathscr{P}}^{(2)j}_{.l} v_m) \right.$$

$$\left. + c^{-1} \varepsilon^{ikl} \frac{\partial}{\partial t} (\bar{\mathscr{P}}^{(2)j}_{.k} B_l) + c^{-1} \varepsilon^{ikl} \nabla_m (v^m \bar{\mathscr{P}}^{(2)j}_{.k} B_l) \right\}$$

($\boldsymbol{\varepsilon}$ is the Levi-Civita tensor).

The 'field' part P^F of the material pressure, occurring in the equation of motion (105), reads in the present case instead of (73)

$$P^{Fij} = -c^{-1} \int \{\hat{v}_1^i \varepsilon^{jkl}(\bar{\mu}_{1k}^{(1)} + \bar{\mu}_{1km}^{(2)} \nabla^m)B_l + \varepsilon_{klm} \bar{\mu}_1^{(2)ik} \hat{v}_1^l \nabla^j B^m\} f_1(R, 1; t) d1.$$

The expression for F shows that the inclusion of quadrupoles has the effect that the force density can no longer be expressed in terms of the Maxwell fields and the complete polarizations: extra terms with the quadrupole densities $\bar{\mathscr{P}}^{(2)}$ and $\bar{\mathscr{M}}^{(2)}$ occur in $\varDelta F$.

4. Consider the double integral

$$\int^{V_1} A(R_1) \cdot \nabla_1 \nabla_1 \cdot \left(\int^{V_2} B(R_2) \frac{1}{4\pi|R_1 - R_2|} dR_2 \right) dR_1. \tag{P1}$$

In particular we want to study the limit of this expression for V_1 and V_2 both tending to a volume V, always keeping V_1 smaller than V_2. Note that the integral may be written also as

$$\int^{V_1} A(R_1) \cdot \nabla_1 \left\{ \mathscr{P} \int^{V_2} B(R_2) \cdot \nabla_1 \frac{1}{4\pi|R_1 - R_2|} dR_2 \right\} dR_1,$$

where the principal value excludes a small volume around R_1 from the integration over R_2. Show that this may be transformed to

$$\mathscr{P} \int^{V_1} \int^{V_2} A(R_1)B(R_2) : \nabla_1 \nabla_1 \frac{1}{4\pi|R_1 - R_2|} dR_1 dR_2$$

$$- \int^{V_1} \left\{ \int^{s_2} A(R_1) \cdot \nabla_1 n_2 \cdot B(R_2) \frac{1}{4\pi|R_1 - R_2|} dS_2 \right\} dR_1,$$

where s_2 is the surface of the small volume excluded in the first integral over R_2. Prove by means of a partial integration and Gauss's theorem that one may write this as

$$-\int^{V_1}\left\{\int^{s_2} A(R_1)\cdot\nabla_1\, n_2\cdot B(R_2)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}S_2\right\}\mathrm{d}R_1$$

$$+\int^{V_1}\int^{V_2}\left[A(R_1)\cdot\nabla_1\{\nabla_2\cdot B(R_2)\}\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_2\right]\mathrm{d}R_1\,,$$

where S_2 is the surface of V_2. Show by another partial integration and application of Gauss's theorem that this expression is equal to:

$$-\int^{S_1}\int^{S_2} n_1\cdot A(R_1)n_2\cdot B(R_2)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}S_1\,\mathrm{d}S_2$$

$$+\int^{V_1}\int^{S_2}\{\nabla_1\cdot A(R_1)\}n_2\cdot B(R_2)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\,\mathrm{d}S_2$$

$$+\int^{S_1}\int^{V_2} n_1\cdot A(R_1)\{\nabla_2\cdot B(R_2)\}\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}S_1\,\mathrm{d}R_2$$

$$-\int^{V_1}\int^{V_2}\{\nabla_1\cdot A(R_1)\}\{\nabla_2\cdot B(R_2)\}\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\,\mathrm{d}R_2\,, \qquad (P2)$$

where (as in all preceding formulae of this problem) the surface and volume of the first integration are smaller than those of the second.

If we had started from the double integral

$$\int^{V_2} B(R_2)\cdot\nabla_2\,\nabla_2\cdot\left(\int^{V_1} A(R_1)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\right)\mathrm{d}R_2 \qquad (P3)$$

with V_1 greater than V_2, we would have found the same result, but with surface and volume of the first integration greater than those of the second. Prove now that in the limit of V_1 and V_2 both tending to V the limit prescriptions – V_1 greater than or smaller than V_2 – give the same result. Hence it is proved now that the limit of the integrals (P1) with $V_1 < V_2$ and (P3) with $V_1 > V_2$ are equal. For that reason this limit is conventionally written as

$$\int\int^{V} A(R_1)B(R_2):\nabla_1\,\nabla_1\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\,\mathrm{d}R_2\,.$$

The same situation occurs in connexion with integrals of the type

$$\int\int^{V_1} B(R_1)\cdot\nabla_1\,\nabla_1\,\nabla_1:\left[\int\int^{V_2}\{A(R_1')-A(R_2)\}C(R_2)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_2\right]$$

$$\delta(R_1-R_1')\mathrm{d}R_1\,\mathrm{d}R_1'$$

with $V_1 < V_2$ and

$$-\int\int^{V_2} C(R_2)\cdot\nabla_2\,\nabla_2\,\nabla_2:\left[\int\int^{V_1}\{A(R_1)-A(R_2')\}B(R_1)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\right]$$

$$\delta(R_2-R_2')\mathrm{d}R_2\,\mathrm{d}R_2'$$

with $V_1 > V_2$ (the reason for the occurrence of the delta function and the extra integration variable being that the functions A are not to be differentiated). These two integrals are equal in the limit V_1, $V_2 \to V$ and are conventionally written as

$$\int\int^{V}\{A(R_1)-A(R_2)\}B(R_1)C(R_2):\nabla_1\nabla_1\,\nabla_1\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\,\mathrm{d}R_2\,,$$

as may be proved along similar lines.

In the main text examples of integrals like the two mentioned here occur frequently. They are always written in the conventional symbolic way, but they must be understood in the sense described above.

However integrals may be considered where the order of integration does matter. An example is given in the next problem.

5. Consider the integral

$$\int^{V_1} A(R_1)\cdot\nabla_1\,\nabla_1\,\nabla_1\cdot\left(\int^{V_2} B(R_2)\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_2\right)\mathrm{d}R_1 \qquad (P4)$$

with $V_1 < V_2$. Prove along the same lines as in the preceding problem that this integral may be written as

$$\int^{V_1} A_{1i}\nabla_1\left(\mathscr{P}\int^{V_2} B_2\cdot\nabla_1\,\nabla_1^i\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_2\right)\mathrm{d}R_1$$

$$-\int^{V_1} A_{1i}\nabla_1\left(\int^{s_2} n_2\cdot B_2\,\nabla_1^i\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}S_2\right)\mathrm{d}R_1\,,$$

where the vector notation could no longer be maintained completely because of the order of the differentiations. The symbols A_1 and B_2 are abbreviations for $A(R_1)$ and $B(R_2)$. Furthermore S_2 is the surface of the small volume around R_1. Partial integration and Gauss's theorem lead to a form

$$-\int^{V_1}\int^{s_2} A_1\cdot\nabla_1\,n_2\cdot B_2\,\nabla_1\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_1\,\mathrm{d}S_2$$

$$+\int^{V_1} A_{1i}\nabla_1\left(\mathscr{P}\int^{V_2}(\nabla_2\cdot B_2)\nabla_1^i\,\frac{1}{4\pi|R_1-R_2|}\,\mathrm{d}R_2\right)\mathrm{d}R_1\,.$$

Show that by taking once more the same steps in the second integral, one arrives at

$$-\int^{S_1}\int^{S_2} n_1 \cdot A_1\, n_2 \cdot B_2\, \nabla_1 \frac{1}{4\pi|R_1-R_2|}\, dS_1\, dS_2$$

$$+\int^{V_1}\int^{S_2} (\nabla_1 \cdot A_1)n_2 \cdot B_2\, \nabla_1 \frac{1}{4\pi|R_1-R_2|}\, dR_1\, dS_2$$

$$-\int^{V_1}\int^{S_2} (\nabla_2 \cdot B_2)n_2\, A_1 \cdot \nabla_1 \frac{1}{4\pi|R_1-R_2|}\, dR_1\, dS_2$$

$$+\int^{V_1}\int^{V_2} \{\nabla_2(\nabla_2 \cdot B_2)\}A_1 \cdot \nabla_1 \frac{1}{4\pi|R_1-R_2|}\, dR_1\, dR_2 \qquad (P5)$$

with V_1 and S_1 smaller than V_2 and S_2.

Check that the integral

$$-\int^{V_2} B(R_2)\cdot\nabla_2\nabla_2\nabla_2\cdot\left(\int^{V_1} A(R_1)\frac{1}{4\pi|R_1-R_2|}\, dR_1\right) dR_2 \qquad (P6)$$

with $V_1 > V_2$ may likewise be written in a form similar to that given in (P5) but with the replacements

$$n_1 \leftrightarrow -n_2, \qquad \nabla_1 \leftrightarrow -\nabla_2, \qquad A_1 \leftrightarrow B_2.$$

Show, by performing repeated partial integrations and employing Gauss's theorem, that one has for the difference of the two integrals (P4) and (P6) in the limit $V_1, V_2 \to V$:

$$\lim_{V_1,V_2\to V}\left\{\int^{V_1(<V_2)} A(R_1)\cdot\nabla_1\nabla_1\nabla_1\cdot\left(\int^{V_2} B(R_2)\frac{1}{4\pi|R_1-R_2|}\, dR_2\right) dR_1\right.$$

$$\left.+\int^{V_2(<V_1)} B(R_2)\cdot\nabla_2\nabla_2\nabla_2\cdot\left(\int^{V_1} A(R_1)\frac{1}{4\pi|R_1-R_2|}\, dR_1\right) dR_2\right\}$$

$$= -\lim_{S_1,S_2\to S}\left(\int\int^{S_1<S_2} - \int\int^{S_1>S_2}\right) n_1 \cdot A_1\, n_2 \cdot B_2\, \nabla_1 \frac{1}{4\pi|R_1-R_2|}\, dS_1\, dS_2. \qquad (P7)$$

Show that the right-hand side of this relation is equal to

$$-\int^{S} n\cdot A\, n\cdot B n\, dS \qquad (P8)$$

by proving first that one has for the integral over an infinite plane S

$$\int^{S} \nabla \frac{1}{4\pi|R-R'|}\, dS = -\tfrac{1}{2}n,$$

where R' is a point outside the plane and n is the normal to the plane pointing in the direction away from R'.

With (P7) and (P8) one may prove now (291) of the main text. Employ to that end in the first term of the left-hand side of (291) the relation (293) together with the expression for the Maxwell field given at the end of problem 1.

Prove finally (243), valid for an ellipsoidal volume, as a particular case of (291). (The pressure P, the polarization P and the deformation $\delta\epsilon$ are all uniform in this case and may be taken outside the integrals.)

6. Show from the integrability relations

$$\frac{\partial P_i}{\partial E_{ej}} = \frac{\partial P_j}{\partial E_{ei}} \qquad (i, j = 1, 2, 3)$$

(v. (380)) and the connexion (220) between the external and Maxwell fields

$$E_e = E + L \cdot P$$

with the symmetrical depolarizing tensor L (219) that one has

$$\frac{\partial P_i}{\partial E_j} = \frac{\partial P_j}{\partial E_i}$$

(v. (383)).

7. Show by introduction of the new integration variables $\check{R} = \tilde{\eta}_A \cdot R$ and the introduction of the abbreviations:

$$\check{P}(\check{R}) \equiv \tilde{\eta}_A \cdot P(R), \qquad \check{M}(\check{R}) \equiv \tilde{\eta}_A \cdot M(R)$$

$$\check{E}(\check{R}) \equiv \tilde{\eta}_A \cdot E(R), \qquad \check{B}(\check{R}) \equiv \tilde{\eta}_A \cdot B(R)$$

$$\check{P}(\check{R}) \equiv \tilde{\eta}_A \cdot P(R) \cdot \eta_A,$$

that the entropy law (317) may be written in the form:

$$T\delta S = \delta U + \int^{\check{S}} n\cdot(\check{P}-\check{P}\cdot\check{E}U)\cdot\delta\eta(R)\cdot R\, dS - \int (\check{E}\cdot\delta_0\check{P}-\check{M}\cdot\delta_0\check{B})dR$$

(where R has been written instead of $\check{R}$ and also δ_0 instead of $\check{\delta}_0$, since they are merely integration variables). This entropy law has the same form as (318) as is to be expected from (305) with (309).

8. In Quincke's experimental arrangement a U-shaped tube with one of its legs inside a condenser is filled with an incompressible, electrically polar-

izable liquid. Show with the help of the formulae (360) and (241) that the difference Δh in height between the two liquid columns is given by

$$\varrho g \Delta h = \tfrac{1}{2}\kappa E^2$$

with ϱ the density, g the acceleration of gravity, κ the electric susceptibility and E the electric field at the surface of the liquid. The liquid inside the condenser has a level higher than on the other side.

9. Prove that the volume average of the pressure tensor in a uniformly polarized solid of ellipsoidal shape is given by

$$\overline{\mathbf{P}} = \mathbf{P}_{\text{out}} - \tfrac{1}{2}\mathbf{K} : \mathbf{PP},$$

if the outward pressure tensor is uniform. In order to prove this, write the components $\bar{P}^{ij}$ of the left-hand side as

$$\bar{P}^{ij} \equiv \frac{1}{V}\int^V P^{kj}\nabla^k R^i \, d\mathbf{R}$$

and apply then a partial integration, Gauss's theorem and the equation of motion $\mathbf{V} \cdot \mathbf{P} = 0$ (v. (293)). The use of the relations (241) and (243) leads then to the right-hand side.

(The form effect of electrostriction described by the first two terms of (390) leads to a non-uniform deformation. The so-called 'uniform form effect' is obtained if one calculates instead the deformation corresponding to the average normal pressure $\mathbf{n} \cdot \overline{\mathbf{P}}$ given above. This calculation is much simpler than that of the non-uniform effect, in particular for more complicated geometries. It gives an estimate of the order of magnitude only.)