THE RELATIVISTIC ENERGY-MOMENTUM TENSOR
IN POLARIZED MEDIA

V. STATISTICAL THERMODYNAMICS OF
ELECTROMAGNETIC PHENOMENA*)

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Synopsis
The relativistic first law of thermodynamics for polarized media is derived from the conservation law of energy-momentum. The nonrelativistic second law for these systems is obtained from equilibrium statistical thermodynamics and generalized to the relativistic case. The entropy balance equation is then derived from the first and second laws.

§ 1. *Introduction*: the energy-momentum conservation laws. The conservation laws of energy and momentum for systems in which the relative atomic motion is nonrelativistic within the correlation domain have the form

$$\partial_\beta(T_{(f)}^{\alpha\beta} + \bar{T}_{(m)}^{\alpha\beta}) = 0, \qquad (\alpha = 0, 1, 2, 3), \tag{1}$$

where a field energy-momentum tensor

$$T_{(f)}^{\alpha\beta} = F^{\alpha\gamma}H^\beta_{\cdot\gamma} - \tfrac{1}{4}F_{\gamma\varepsilon}F^{\gamma\varepsilon}g^{\alpha\beta} +$$
$$+ c^{-2}U^\beta(F^{\alpha\gamma}M_{\gamma\varepsilon} - M^{\alpha\gamma}F_{\gamma\varepsilon})U^\varepsilon - c^{-4}U^\alpha U^\beta U^\gamma F_{\gamma\varepsilon}M^{\varepsilon\zeta}U_\zeta \tag{2}$$

has been introduced[1]). The corresponding material energy-momentum tensor $\bar{T}_{(m)}^{\alpha\beta}$ was given as a statistical expression in terms of characteristic atomic parameters[1]). The laws (1) will form the basis of the thermodynamic considerations of this paper.

§ 2. *The relativistic first law of thermodynamics.* If the conservation law (1) is multiplied by the macroscopic four-velocity U_α, which was defined[1]) as the average atomic velocity, one gets the equation

$$U_\alpha\partial_\beta(T_{(f)}^{\alpha\beta} + \bar{T}_{(m)}^{\alpha\beta}) = 0. \tag{3}$$

The material energy-momentum tensor, which in the local momentary

rest frame has equal time-space and space-time components[1]), may be written as

$$\bar{T}^{\alpha\beta}_{(m)} = c^{-2} U^{\alpha} U^{\beta} (\varrho' c^2 + e'_v) + c^{-2} (U^{\alpha} I^{\beta} + I^{\alpha} U^{\beta}) + P^{\beta\alpha}, \qquad (4)$$

where a scalar energy density e'_v, a heat flow four-vector I^{α} and a pressure four-tensor $P^{\alpha\beta}$ are introduced. They are defined as

$$e'_v = c^{-2} U_{\alpha} U_{\beta} \bar{T}^{\alpha\beta}_{(m)} - \varrho' c^2, \qquad (5)$$

$$I^{\alpha} = -U_{\beta} \bar{T}^{\beta\gamma}_{(m)} \Delta^{\alpha}_{\gamma} = -\Delta^{\alpha}_{\beta} \bar{T}^{\beta\gamma}_{(m)} U_{\gamma}, \qquad (6)$$

$$P^{\alpha\beta} = \Delta^{\alpha}_{\gamma} \Delta^{\beta}_{\varepsilon} \bar{T}^{\varepsilon\gamma}_{(m)}. \qquad (7)$$

Here Δ^{α}_{β} stands for $\delta^{\alpha}_{\beta} + c^{-2} U^{\alpha} U_{\beta}$ and ϱ' is the rest mass density in the rest frame, which obeys the conservation law

$$\partial_{\alpha} (\varrho' U^{\alpha}) = 0. \qquad (8)$$

Since in the rest frame U^{α} has the form $(c, 0, 0, 0)$ the four-vector I^{α} and the four-tensor $P^{\alpha\beta}$ are purely space-like.

The expressions (2) and (4) will be introduced into the law (3). The polarization tensor $M^{\alpha\beta}$, which occurs in (2), is split into two parts

$$M^{\alpha\beta} = M^{(1)\alpha\beta} + M^{(2)\alpha\beta}, \qquad (9)$$

where

$$M^{(1)\alpha\beta} = -c^2 (U^{\alpha} U_{\gamma} M^{\gamma\beta} + U^{\beta} U_{\gamma} M^{\alpha\gamma}), \qquad (10)$$

$$M^{(2)\alpha\beta} = \Delta^{\alpha}_{\gamma} \Delta^{\beta}_{\varepsilon} M^{\gamma\varepsilon}. \qquad (11)$$

From these definitions the properties

$$\Delta^{\alpha}_{\gamma} \Delta^{\beta}_{\varepsilon} M^{(1)\gamma\varepsilon} = 0, \qquad (12)$$

$$U_{\alpha} M^{(2)\alpha\beta} = 0 \qquad (13)$$

follow. Therefore in the rest frame the only non-vanishing components of $M^{(1)\alpha\beta}$ are space-time-like, while $M^{(2)\alpha\beta}$ is then purely space-space-like. Thus (in the rest frame) $M^{(1)\alpha\beta}$ and $M^{(2)\alpha\beta}$ represent the electric and magnetic polarization respectively.

The first term of (3) becomes with (2), (8)–(11) and the Maxwell equations

$$U_{\alpha} \partial_{\beta} T^{\alpha\beta}_{(f)} = -c^{-1} U_{\alpha} F^{\alpha\beta} J_{\beta} + \tfrac{1}{2} F'_{\alpha\beta} \varrho' D(v' M^{(1)\alpha\beta'}) - \tfrac{1}{2} M^{(2)'}_{\alpha\beta} D F^{\alpha\beta'}, \qquad (14)$$

where J^{α} is the macroscopic four-current, $v' = (\varrho')^{-1}$ and $D = U_{\alpha} \partial^{\alpha}$. The dash denotes quantities in the local rest frame; for arbitrary antisymmetric tensors $A^{\alpha\beta}$ and $B^{\alpha\beta}$ one has

$$A'_{\alpha\beta} D B^{\alpha\beta'} = A_{\alpha\beta} D B^{\alpha\beta} + 2c^{-2} U^{\alpha} (A_{\alpha\beta} B^{\beta\gamma} - B_{\alpha\beta} A^{\beta\gamma}) D U_{\gamma}. \qquad (15)$$

The second term of (3) becomes with (4) and (8)

$$U_{\alpha} \partial_{\beta} \bar{T}^{\alpha\beta}_{(m)} = -\varrho' D e' - (\partial_{\alpha} I^{\alpha} + c^{-2} I^{\alpha} D U_{\alpha}) - P^{\alpha\beta} \partial_{\alpha} U_{\beta}, \qquad (16)$$

where $e' = v'e'_v$ is the energy per unit rest mass. The law (3) reads with (14) and (16)

$$\varrho'De' = -(\partial_\alpha I^\alpha + c^{-2} I^\alpha D U_\alpha) - P^{\alpha\beta}\partial_\alpha U_\beta - c^{-1}U_\alpha F^{\alpha\beta}J_\beta +$$
$$+ \tfrac{1}{2}F'_{\alpha\beta}\varrho'D(v'M^{(1)\alpha\beta'}) - \tfrac{1}{2}M^{(2)'}_{\alpha\beta}DF^{\alpha\beta'}. \quad (17)$$

This is the first law of relativistic thermodynamics for polarized media. It gives an expression for the change in time of the energy e'. The right-hand side contains in the first place the divergence of the heat flow I^α together with Eckart's[2]) relativistic correction, and a term with the pressure tensor $P^{\alpha\beta}$. Furthermore terms with the electromagnetic field $F^{\alpha\beta}$, the four-current density J^α and the polarizations $M^{(1)\alpha\beta}$ and $M^{(2)\alpha\beta}$ occur.

§ 3. *The second law of thermodynamics in nonrelativistic approximation.* In this section we shall derive the nonrelativistic second law for dipole substances from equilibrium statistics with the help of the canonical ensemble[3]). In the following section a relativistic second law will be introduced as a generalization of the nonrelativistic law.

The system, which in general is not uniform, will be considered as the union of a number of cells, each of which contains on the one hand a large number of atoms (or molecules), so that the principles of statistical mechanics may be applied, but is on the other hand sufficiently small to be considered macroscopically uniform. The shape of the cells will be chosen ellipsoidal since then uniform external fields produce uniform polarizations. The bulk velocity in the cell will be taken equal to zero. Furthermore the system will be supposed to have a correlation length which is small compared to the dimensions of the cell. This is the case in fluid systems to which we shall confine our discussion. Finally we shall consider only substances in which the mechanical effects due to the atomic angular momenta are negligible.

From the expression (A 9) with (A 5), (A 6) (v. appendix I) for the Hamiltonian H of the atoms k with electric dipole moments μ_k and magnetic dipole moments ν_k contained in a cell the macroscopic energy follows by averaging:

$$\langle H \rangle = \langle K \rangle + \left\langle \tfrac{1}{2}\sum_{k}\sum_{i,j,i\neq j} \frac{e_{ki}e_{kj}}{4\pi|r_{ki} - r_{kj}|} \right\rangle$$
$$+ \left\langle \tfrac{1}{2}\sum_{k,l,k\neq l} \mu_k \cdot \nabla_{R_k}\mu_l \cdot \nabla_{R_l} \frac{1}{4\pi|R_k - R_l|} \right\rangle$$
$$- \left\langle \tfrac{1}{2}\sum_{k,l,k\neq l} \nu_k \cdot \nabla_{R_k}\nu_l \cdot \nabla_{R_l} \frac{1}{4\pi|R_k - R_l|} \right\rangle - \left\langle \sum_{k} \mu_k \cdot E^{(e)}(R_k) \right\rangle, \quad (18)$$

where K is the kinetic energy. One can write this alternatively using the one-point distribution function $f_1(R_1, \mu_1; t)$ and the two-point distribution

functions $f_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t)$ and $f_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t)$, as

$$\langle H \rangle = \langle K \rangle + \tfrac{1}{2} \left\langle \sum_k \sum_{i,j,i \neq j} \frac{e_{ki}e_{kj}}{4\pi |\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|} \right\rangle$$

$$+ \tfrac{1}{2} \int \left(\boldsymbol{\mu}_1 \cdot \boldsymbol{\nabla}_{R_1} \boldsymbol{\mu}_2 \cdot \boldsymbol{\nabla}_{R_2} \frac{1}{4\pi |\boldsymbol{R}_1 - \boldsymbol{R}_2|} \right) f_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t)\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2\, \mathrm{d}\boldsymbol{\mu}_1\, \mathrm{d}\boldsymbol{\mu}_2$$

$$- \tfrac{1}{2} \int \left(\boldsymbol{\nu}_1 \cdot \boldsymbol{\nabla}_{R_1} \boldsymbol{\nu}_2 \cdot \boldsymbol{\nabla}_{R_2} \frac{1}{4\pi |\boldsymbol{R}_1 - \boldsymbol{R}_2|} \right) f_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t)\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2\, \mathrm{d}\boldsymbol{\nu}_1\, \mathrm{d}\boldsymbol{\nu}_2$$

$$- \int \boldsymbol{\mu}_1 \cdot \boldsymbol{E}^{(e)}(\boldsymbol{R}_1)\, f_1(\boldsymbol{R}_1, \boldsymbol{\mu}_1; t)\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{\mu}_1, \tag{19}$$

where the volume integrations are extended over the cell. Introducing the correlation function

$$c_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t) = f_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t) - f_1(\boldsymbol{R}_1, \boldsymbol{\mu}_1; t)\, f_1(\boldsymbol{R}_2, \boldsymbol{\mu}_2; t) \tag{20}$$

and a similar function $\boldsymbol{\nu}_1$ and $\boldsymbol{\nu}_2$, one gets for (19)

$$\langle H \rangle = \langle K \rangle + \tfrac{1}{2} \left\langle \sum_k \sum_{i,j,i \neq j} \frac{e_{ki}e_{kj}}{4\pi |\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|} \right\rangle$$

$$+ \tfrac{1}{2} \int \left((\boldsymbol{\mu}_1 \cdot \boldsymbol{\nabla}_{R_1} \boldsymbol{\mu}_2 \cdot \boldsymbol{\nabla}_{R_2} \frac{1}{4\pi |\boldsymbol{R}_1 - \boldsymbol{R}_2|} \right) c_2(\boldsymbol{R}_1, \boldsymbol{R}_2\, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t)\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2\, \mathrm{d}\boldsymbol{\mu}_1\, \mathrm{d}\boldsymbol{\mu}_2$$

$$- \tfrac{1}{2} \int \left(\boldsymbol{\nu}_1 \cdot \boldsymbol{\nabla}_{R_1} \boldsymbol{\nu}_2 \cdot \boldsymbol{\nabla}_{R_2} \frac{1}{4\pi |\boldsymbol{R}_1 - \boldsymbol{R}_2|} \right) c_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t)\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2\, \mathrm{d}\boldsymbol{\nu}_1\, \mathrm{d}\boldsymbol{\nu}_2$$

$$+ \tfrac{1}{2}(\boldsymbol{PP} - \boldsymbol{MM}): \int \boldsymbol{\nabla}_{R_1} \boldsymbol{\nabla}_{R_2} \frac{1}{4\pi |\boldsymbol{R}_1 - \boldsymbol{R}_2|}\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2 - V\boldsymbol{P} \cdot \boldsymbol{E}^{(e)}, \tag{21}$$

where V is the volume of the cell and where

$$\boldsymbol{P} = \int \boldsymbol{\mu}_1 f_1(\boldsymbol{R}, \boldsymbol{\mu}_1; t)\, \mathrm{d}\boldsymbol{\mu}_1, \tag{22}$$

$$\boldsymbol{M} = \int \boldsymbol{\nu}_1 f_1(\boldsymbol{R}, \boldsymbol{\nu}_1; t)\, \mathrm{d}\boldsymbol{\nu}_1 \tag{23}$$

are the macroscopic polarizations, which are uniform over the cell. Since the system in the cell is assumed to be uniform the correlation functions $c_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t)$ and $c_2(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t)$ depend on $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ only through their difference $\boldsymbol{s} = \boldsymbol{R}_1 - \boldsymbol{R}_2$; in the third and fourth term of $\langle H \rangle$ we shall write $c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t)$ and $c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t)$ where $\boldsymbol{R}$ is an arbitrary position within the cell. As is shown in appendix III one has for the integral in the fifth term:

$$\int \boldsymbol{\nabla}_{R_1} \boldsymbol{\nabla}_{R_2} \frac{1}{4\pi |\boldsymbol{R}_1 - \boldsymbol{R}_2|}\, \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2 = -V \int \boldsymbol{\nabla}_s \boldsymbol{\nabla}_s \frac{1}{4\pi s}\, \mathrm{d}\boldsymbol{s}, \tag{24}$$

where s is the position vector measured from the centre of the ellipsoidal cell. The right-hand side contains the *depolarization tensor*

$$\mathbf{L}(\boldsymbol{\epsilon}) = -\int \boldsymbol{V}_s \boldsymbol{V}_s \frac{1}{4\pi s} \, \mathrm{d}s, \tag{25}$$

which depends on the (uniform) deformation tensor $\boldsymbol{\epsilon}$ of the ellipsoidal cell. In this way (21) becomes

$$\langle H \rangle = \langle K \rangle + \tfrac{1}{2} \left\langle \sum_k \sum_{i,j,i\neq j} \frac{e_{ki}e_{kj}}{4\pi|\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|} \right\rangle$$

$$- \tfrac{1}{2}V\int \left(\boldsymbol{\mu}_1 \cdot \boldsymbol{V}_s \boldsymbol{\mu}_2 \cdot \boldsymbol{V}_s \frac{1}{4\pi s} \right) c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t) \, \mathrm{d}s \, \mathrm{d}\boldsymbol{\mu}_1 \, \mathrm{d}\boldsymbol{\mu}_2$$

$$+ \tfrac{1}{2}V\int \left(\boldsymbol{\nu}_1 \cdot \boldsymbol{V}_s \boldsymbol{\nu}_2 \cdot \boldsymbol{V}_s \frac{1}{4\pi s} \right) c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t) \, \mathrm{d}s \, \mathrm{d}\boldsymbol{\nu}_1 \, \mathrm{d}\boldsymbol{\nu}_2$$

$$+ \tfrac{1}{2}V\mathbf{L}(\boldsymbol{\epsilon}) : (\boldsymbol{PP} - \boldsymbol{MM}) - V\boldsymbol{P} \cdot \boldsymbol{E}^{(e)}. \tag{26}$$

Terms of this energy expression occur in the nonrelativistic energy law (IV.55–56), of which the left-hand side reads, using (IV.20) and (IV.67):

$$(\partial/\partial t)(\overline{T}_{(m)}^{00} - \varrho c^2) + V_i(c\overline{T}_{(m)}^{0i} - \varrho c^2 v^i), \tag{27}$$

where the energy density $\overline{T}_{(m)}^{00} - \varrho c^2 \equiv e_v'$ (5) (for neutral atoms with negligible angular momenta and $v = 0$) was given by

$$e_v' = \delta\varrho c^2 + \int \tfrac{1}{2}m_1 \hat{v}_1^2 f_1(\boldsymbol{R}, \boldsymbol{v}_1; t) \, \mathrm{d}\boldsymbol{v}_1$$

$$- \tfrac{1}{2}\int \left(\boldsymbol{\mu}_1 \cdot \boldsymbol{V}_s \boldsymbol{\mu}_2 \cdot \boldsymbol{V}_s \frac{1}{4\pi s} \right) c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2; t) \, \mathrm{d}s \, \mathrm{d}\boldsymbol{\mu}_1 \, \mathrm{d}\boldsymbol{\mu}_2$$

$$- \tfrac{1}{2}\int \left\{ (\boldsymbol{\nu}_1 \wedge \boldsymbol{V}_s)(\boldsymbol{\nu}_2 \wedge \boldsymbol{V}_s) : \frac{\mathbf{T}(s)}{8\pi s} \right\} c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t) \, \mathrm{d}s \, \mathrm{d}\boldsymbol{\nu}_1 \, \mathrm{d}\boldsymbol{\nu}_2, \tag{28}$$

where $\mathbf{T}(s) = \mathbf{U} + \boldsymbol{ss}/s^2$ ($\mathbf{U}$ is the unit tensor). With the help of (IV.A 1), (IV.A 2), (IV.A 13), (IV.70) and (23) the last term of this expression may be transformed into:

$$\tfrac{1}{2}\int \left(\boldsymbol{\nu}_1 \cdot \boldsymbol{V}_s \boldsymbol{\nu}_2 \cdot \boldsymbol{V}_s \frac{1}{4\pi s} \right) c_2(\boldsymbol{R} + \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{R} - \tfrac{1}{2}\boldsymbol{s}, \boldsymbol{\nu}_1, \boldsymbol{\nu}_2; t) \, \mathrm{d}s \, \mathrm{d}\boldsymbol{\nu}_1 \, \mathrm{d}\boldsymbol{\nu}_2 - \tfrac{1}{2}M^2, \tag{29}$$

where the first term has the same form as the electric dipole term in (28). Comparing (28), (29) with expression (26) one has:

$$\langle H \rangle = V\{e_v' + \tfrac{1}{2}\mathbf{L}(\boldsymbol{\epsilon}) : (\boldsymbol{PP} - \boldsymbol{MM}) - \boldsymbol{P} \cdot \boldsymbol{E}^{(e)} + \tfrac{1}{2}M^2\}. \tag{30}$$

The canonical ensemble, which describes the cell in equilibrium, is given

by the distribution function

$$f = C\, e^{(F-H)/kT},\qquad (31)$$

where $H(q, p)$ is given by (A 10) and where C is a constant (depending on the number of atoms). The free energy

$$F = \langle H \rangle - TS \qquad (32)$$

of a one-component system*) is a function of the independent variables: the deformation tensor ϵ_{ij}, the external fields $\boldsymbol{E}^{(e)}$ and $\boldsymbol{B}^{(e)}$ and the temperature T:

$$dF = \frac{\partial F}{\partial \boldsymbol{\epsilon}} : d\widetilde{\boldsymbol{\epsilon}} + \frac{\partial F}{\partial \boldsymbol{E}^{(e)}} \cdot d\boldsymbol{E}^{(e)} + \frac{\partial F}{\partial \boldsymbol{B}^{(e)}} \cdot d\boldsymbol{B}^{(e)} + \frac{\partial F}{\partial T}\, dT. \qquad (33)$$

The partial derivative $\partial F/\partial T$ gives the entropy: $S = -\partial F/\partial T$. From (31) and (A 10) it follows that

$$(\partial F)/\partial \boldsymbol{E}^{(e)})_{\widetilde{\boldsymbol{\epsilon}}_{ij}, \boldsymbol{B}^{(e)}, T} = -\langle \sum_k \boldsymbol{\mu}_k \rangle = -V\boldsymbol{P}, \qquad (34)$$

$$(\partial F/\partial \boldsymbol{B}^{(e)})_{\boldsymbol{\epsilon}_{ij}, \boldsymbol{B}^{(e)}, T} = -\langle \sum_k \boldsymbol{\nu}_k \rangle = -V\boldsymbol{M}. \qquad (35)$$

From (32) and (33) one proves that

$$(\partial F/\partial \boldsymbol{\epsilon})_{\boldsymbol{E}^{(e)}, \boldsymbol{B}^{(e)}, T} = (\partial \langle H \rangle/\partial \boldsymbol{\epsilon})_{\boldsymbol{E}^{(e)}, \boldsymbol{B}^{(e)}, S} . \qquad (36)$$

From a consideration of the work exerted on the system (see appendix II), it follows that the last formula may be written as

$$\left(\frac{\partial F}{\partial \boldsymbol{\epsilon}} \right)_{\boldsymbol{E}^{(e)}, \boldsymbol{B}^{(e)}, T} = -\left\langle \sum_k \left(\frac{\partial H}{\partial \boldsymbol{P}_k} \right) \boldsymbol{P}_k - \boldsymbol{R}_k \frac{\partial H}{\partial \boldsymbol{R}_k} \right\rangle. \qquad (37)$$

With (A.10) this becomes, since one has $\boldsymbol{p}_{k1} \equiv \boldsymbol{P}_k = m_k \dot{\boldsymbol{R}}_k$:

$$\left(\frac{\partial F}{\partial \boldsymbol{\epsilon}} \right)_{\boldsymbol{E}^{(e)}, \boldsymbol{B}^{(e)}, T} = -\langle \sum_k m_k \dot{\boldsymbol{R}}_k \dot{\boldsymbol{R}}_k \rangle$$

$$+ \left\langle \sum_{k, l, k \neq l} \boldsymbol{R}_k \boldsymbol{\nabla}_{\boldsymbol{R}_k} \boldsymbol{\mu}_k \cdot \boldsymbol{\nabla}_{\boldsymbol{R}_k} \boldsymbol{\mu}_l \cdot \boldsymbol{\nabla}_{\boldsymbol{R}_l} \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|} \right\rangle$$

$$+ \left\langle \sum_{k, l, k \neq l} \boldsymbol{R}_k \boldsymbol{\nabla}_{\boldsymbol{R}_k} \boldsymbol{\nu}_k \cdot \boldsymbol{\nabla}_{\boldsymbol{R}_k} \boldsymbol{\nu}_l \cdot \boldsymbol{\nabla}_{\boldsymbol{R}_l} \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|} \right\rangle, \qquad (38)$$

where use has been made of the fact that $\boldsymbol{E}^{(e)}$ and $\boldsymbol{B}^{(e)}$ are uniform over the cell. Using distribution functions just as in the derivation of (21) one gets

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*) The generalization to mixtures consists merely in adding a term containing the chemical potentials and the composition parameters to the right-hand side of (33).

for (38)

$$\left(\frac{\partial F}{\partial \epsilon}\right)_{E^{(e)},\,B^{(e)},\,T} = -\int m_1 v_1 v_1 f_1(\mathbf{R}_1,\,\mathbf{v}_1;\,t)\,\mathrm{d}\mathbf{R}_1\,\mathrm{d}\mathbf{v}_1$$

$$+\int\left(\mathbf{R}_1\nabla_{R_1}\boldsymbol{\mu}_1\cdot\nabla_{R_1}\boldsymbol{\mu}_2\cdot\nabla_{R_2}\frac{1}{4\pi|\mathbf{R}_1-\mathbf{R}_2|}\right)c_2(\mathbf{R}_1,\,\mathbf{R}_2,\,\boldsymbol{\mu}_1,\,\boldsymbol{\mu}_2;\,t)\,\mathrm{d}\mathbf{R}_1\,\mathrm{d}\mathbf{R}_2\,\mathrm{d}\boldsymbol{\mu}_1\,\mathrm{d}\boldsymbol{\mu}_2$$

$$+\int\left(\mathbf{R}_1\nabla_{R_1}\boldsymbol{\nu}_1\cdot\nabla_{R_1}\boldsymbol{\nu}_2\cdot\nabla_{R_2}\frac{1}{4\pi|\mathbf{R}_1-\mathbf{R}_2|}\right)c_2(\mathbf{R}_1,\,\mathbf{R}_2,\,\boldsymbol{\nu}_1,\,\boldsymbol{\nu}_2;\,t)\,\mathrm{d}\mathbf{R}_1\,\mathrm{d}\mathbf{R}_2\,\mathrm{d}\boldsymbol{\nu}_1\,\mathrm{d}\boldsymbol{\nu}_2$$

$$+\left(\int\mathbf{R}_1\nabla_{R_1}\nabla_{R_1}\nabla_{R_2}\frac{1}{4\pi|\mathbf{R}_1-\mathbf{R}_2|}\,\mathrm{d}\mathbf{R}_1\,\mathrm{d}\mathbf{R}_2\right):(\mathbf{PP}+\mathbf{MM}),\tag{39}$$

As is shown in appendix III one has for the integral in the fourth term:

$$\int\mathbf{R}_1\nabla_{R_1}\nabla_{R_1}\nabla_{R_2}\frac{1}{4\pi|\mathbf{R}_1-\mathbf{R}_2|}\,\mathrm{d}\mathbf{R}_1\,\mathrm{d}\mathbf{R}_2 = -\tfrac{1}{2}V\int s\nabla_s\nabla_s\nabla_s\frac{1}{4\pi s}\,\mathrm{d}s,\tag{40}$$

where s is the position vector measured from the centre of the ellipsoidal cell. The right-hand side contains the tensor of the fourth rank:

$$\mathbf{K}(\epsilon) = \int s\nabla_s\nabla_s\nabla_s\frac{1}{4\pi s}\,\mathrm{d}s.\tag{41}$$

Introducing into (39) the relative coordinates s and using the uniformity of the distribution functions, one gets

$$\left(\frac{\partial F}{\partial \epsilon}\right)_{E^{(e)},\,B^{(e)},\,T} = -V\int m_1 v_1 v_1 f_1(\mathbf{R},\,\mathbf{v}_1;\,t)\,\mathrm{d}\mathbf{v}_1$$

$$-\tfrac{1}{2}V\int\left(s\nabla_s\boldsymbol{\mu}_1\cdot\nabla_s\boldsymbol{\mu}_2\cdot\nabla_s\frac{1}{4\pi s}\right)c_2(\mathbf{R}+\tfrac{1}{2}s,\,\mathbf{R}-\tfrac{1}{2}s,\,\boldsymbol{\mu}_1,\,\boldsymbol{\mu}_2;\,t)\,\mathrm{d}s\,\mathrm{d}\boldsymbol{\mu}_1\,d\boldsymbol{\mu}_2$$

$$-\tfrac{1}{2}V\int\left(s\nabla_s\boldsymbol{\nu}_1\cdot\nabla_s\boldsymbol{\nu}_2\cdot\nabla_s\frac{1}{4\pi s}\right)c_2(\mathbf{R}+\tfrac{1}{2}s,\,\mathbf{R}-\tfrac{1}{2}s,\,\boldsymbol{\nu}_1,\,\boldsymbol{\nu}_2;\,t)\,\mathrm{d}s\,\mathrm{d}\boldsymbol{\nu}_1\,\mathrm{d}\boldsymbol{\nu}_2$$

$$-\tfrac{1}{2}V\mathbf{K}(\epsilon):(\mathbf{PP}+\mathbf{MM}).\tag{42}$$

Apart from a factor $(-V)$ terms of the right-hand side occur in the non-relativistic momentum law (IV.58–59) of which the left-hand side is

$$c^{-1}(\partial/\partial t)\,\overline{T}^{j0}_{(m)} + \nabla_i\overline{T}^{ji}_{(m)},\tag{43}$$

where the pressure $\overline{T}^{ij}_{(m)} = P^{ji}$ for the dipole substance in rest $(\mathbf{v} = \mathbf{v}_1 -$

$- \hat{v}_1 = 0$) is

$$P = \int m_1 v_1 v_1 f_1(R, v_1; t) \, dv_1$$

$$+ \tfrac{1}{2} \int \left(s \nabla_s \mu_1 \cdot \nabla_s \mu_2 \cdot \nabla_s \frac{1}{4\pi s} \right) c_2(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s, \mu_1, \mu_2; t) \, ds \, d\mu_1 \, d\mu_2$$

$$- \tfrac{1}{2} \int \left\{ s \nabla_s (v_1 \wedge \nabla_s)(v_2 \wedge \nabla_s) : \frac{T(s)}{8\pi s} \right\} c_2(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s, v_1, v_2; t) \, ds \, dv_1 \, dv_2,$$

$$(44)$$

where the effect of atomic angular momenta have again been neglected. With the help of (IV.A 3). IV.A 4), (IV.A 13), (IV. 70) and (23) the last term of this expression may be transformed into:

$$\tfrac{1}{2} \int \left((s \nabla_s v_1 \cdot \nabla_s v_2 \cdot \nabla_s \frac{1}{4\pi s} \right) c_2(R + \tfrac{1}{2}s, R - \tfrac{1}{2}s, v_1, v_2; t) \, ds \, dv_1 \, dv_2 + \tfrac{1}{2} M^2 U. \quad (45)$$

With the tensor (44)–(45) the expression (42) becomes:

$$\left(\frac{\partial F}{\partial \epsilon} \right)_{E^{(e)}, B^{(e)}, T} = -V\{P + \tfrac{1}{2}K(\epsilon) : (PP + MM) - \tfrac{1}{2}M^2 U\}. \quad (46)$$

With (34), (35) and (46) the total derivative (33) of the free energy gets the form:

$$dF = -V\{P + \tfrac{1}{2}K(\epsilon) : (PP + MM) - \tfrac{1}{2}M^2 U\} : d\tilde{\epsilon} -$$
$$- VP \cdot dE^{(e)} - VM \cdot dB^{(e)} - S \, dT, \quad (47)$$

where $\tilde{\epsilon}$ is the transposed tensor of ϵ. From this expression with (30) and (32) one gets for the specific entropy $s = S/M$ (with M the mass in the cell):

$$T \, ds = d\{e + \tfrac{1}{2}vL(\epsilon) : (PP - MM) + \tfrac{1}{2}vM^2\} +$$
$$+ v\{P + \tfrac{1}{2}K(\epsilon) : (PP + MM) - \tfrac{1}{2}M^2 U\} : d\tilde{\epsilon} - E^{(e)} \cdot d(vP) + vM \cdot dB^{(e)}, \quad (48)$$

where e is the specific energy ve'_v and $v = V/M$ the specific volume. For the (ellipsoidal) cell the Maxwell fields E and B are

$$E = E^{(e)} - L(\epsilon) \cdot P, \quad B = B^{(e)} - L(\epsilon) \cdot M + M. \quad (49)$$

These relations permit us to express the external fields in terms of the local fields E, B, P, M and the deformation tensor ϵ. Equation (48) becomes then:

$$T \, ds = de + vP : d\tilde{\epsilon} - E \cdot d(vP) + vM \cdot dB$$
$$+ d\{\tfrac{1}{2}vL(\epsilon) : (PP - MM) + \tfrac{1}{2}vM^2\} + \tfrac{1}{2}v\{K(\epsilon) : (PP + MM) - M^2 U\} : d\tilde{\epsilon}$$
$$- P \cdot L(\epsilon) \cdot d(vP) + vM \cdot d\{L(\epsilon) \cdot M - M\}. \quad (50)$$

Since $\mathbf{U} : d\boldsymbol{\epsilon}$ is equal to $v^{-1} dv$ the second and third lines are:

$$d\{\tfrac{1}{2}v\mathbf{L}(\boldsymbol{\epsilon}) : (\boldsymbol{PP} + \boldsymbol{MM}\} + \tfrac{1}{2}v\{\mathbf{K}(\boldsymbol{\epsilon}) : (\boldsymbol{P\dot{P}} + \boldsymbol{MM})\} : d\tilde{\boldsymbol{\epsilon}}$$

$$- \boldsymbol{P} \cdot \mathbf{L}(\boldsymbol{\epsilon}) \cdot d(v\boldsymbol{P}) - \boldsymbol{M} \cdot \mathbf{L}(\boldsymbol{\epsilon}) \cdot d(v\boldsymbol{M}). \tag{51}$$

As shown in appendix III one may prove the identity:

$$\frac{\partial}{\partial \boldsymbol{\epsilon}} \{v^{-1}\mathbf{L}(\boldsymbol{\epsilon})\} = -v^{-1}\mathbf{K}(\boldsymbol{\epsilon}), \tag{52}$$

so that the expression (51) vanishes. The relation (50) becomes now:

$$T \, ds = de + v\boldsymbol{P} : d\tilde{\boldsymbol{\epsilon}} - \boldsymbol{E} \cdot d(v\boldsymbol{P}) + v\boldsymbol{M} \cdot d\boldsymbol{B}, \tag{53}$$

where now only *local* quantities occur. The differential relations, such as (53), should be understood as relations between time derivatives. For that reason we shall write from now on D, which stands for d/dt, instead of d. (We note that $D\boldsymbol{\epsilon}$ is equal to $\boldsymbol{\nabla}\boldsymbol{v}$, where $\boldsymbol{v}$ is the velocity).

Fluid systems are (by definition) isotropic in the absence of polarization. Futhermore the polarization vectors $\boldsymbol{P}$ and $\boldsymbol{M}$ will be parallel to $\boldsymbol{E}$ and $\boldsymbol{B}$, and functions of the density $\varrho = v^{-1}$, the specific entropy s (or temperature) and the fields $\boldsymbol{E}$ and $\boldsymbol{B}$ respectively. Now (53) can be integrated at constant $\boldsymbol{\epsilon}$ and s[4]). This yields the energy e in the form

$$e = e^0 + \Delta e, \tag{54}$$

where e^0 is the energy at zero polarization, which depends only on ϱ and s, while Δe is a function of ϱ, s, $\boldsymbol{E}^2$ and $\boldsymbol{B}^2$, or of ϱ, s, $\boldsymbol{P}^2$ and $\boldsymbol{B}^2$. Therefore $D e$ contains only the trace of $D\boldsymbol{\epsilon}$ which is equal to $\boldsymbol{\nabla} \cdot \boldsymbol{v} = -\varrho^{-1}D\varrho$. From (53) it follows now that in the equilibrium state of the fluid the tensor $\boldsymbol{P}$ reduces to a *scalar* pressure p, multiplied by the unit tensor. In this way (53) becomes

$$TDs = De + pDv - \boldsymbol{E} \cdot D(v\boldsymbol{P}) + v\boldsymbol{M} \cdot D\boldsymbol{B}, \tag{55}$$

which is the *nonrelativistic second law* (Gibbs relation) *for (one-component) polarized fluids*.

§ 4. *The relativistic second law*. In the preceding section the nonrelativistic second law (55) has been derived for fluid systems in equilibrium. This law contains the specific energy e and the pressure p which are connected to quantities appearing in (27) and (43):

$$e = v\bar{T}^{00}_{(m)} - c^2, \tag{56}$$

$$p = \bar{T}^{11}_{(m)} = \bar{T}^{22}_{(m)} = \bar{T}^{33}_{(m)}. \tag{57}$$

All quantities occurring here are defined in the local rest frame; we shall mark them from now on by primes.

Since no statistical derivation of a second law for relativistic systems (with interaction) in equilibrium is available, we postulate in analogy with the nonrelativistic law (55):

$$T'Ds' = De' + p'Dv' - \boldsymbol{E}'.D(v'\boldsymbol{P}') + v'\boldsymbol{M}'\cdot D\boldsymbol{B}' \tag{58}$$

as the relativistic second law (,,Gibbs relation'') for neutral polarized fluids locally in equilibrium. The quantities with primes are defined in the local permanent rest frame in which the system is locally at rest all the time. (The permanent rest frame is a succession of Lorentz frames, not a Lorentz frame itself). The derivative D stands for $U^\alpha \partial_\alpha$ where U^α is the local macroscopic four-velocity; it is the time derivative $\mathrm{d}/\mathrm{d}t'$ in the local rest frame. Since $\boldsymbol{E}'$ and $\boldsymbol{B}'$ form the tensor $F'_{\alpha\beta}$, and $\boldsymbol{P}'$ and $\boldsymbol{M}'$ the tensor $M'_{\alpha\beta}$ we may rewrite (58) with the help of (9)–(11) as

$$T'Ds' = De' + p'Dv' - \tfrac{1}{2}F'_{\alpha\beta}D(v'M^{(1)\alpha\beta'}) + \tfrac{1}{2}v'M^{(2)'}_{\alpha\beta}DF^{\alpha\beta'} \tag{59}$$

This is the relativistic second law in covariant form.

From the combination of the first and second laws the relativistic entropy balance equation for a neutral (and current-free) polarized fluid may be obtained. In fact from (17) and (59) it follows that

$$\varrho'Ds' = -\partial_\alpha S^\alpha + \sigma, \tag{60}$$

where we introduced the entropy flux

$$S^\alpha \equiv I^\alpha/T' \tag{61}$$

and the entropy source strength

$$\sigma \equiv \frac{1}{T'}\left\{ -I^\alpha\left(\frac{1}{T'}\,\partial_\alpha T' + c^{-2}DU_\alpha\right) - (P^{\alpha\beta} - p'\Delta^{\alpha\beta})\,\partial_\alpha U_\beta \right\}. \tag{62}$$

The entropy flux (61) is equal to the heat flow I^α divided by the temperature. In the entropy production (62) contributions from heat conduction and viscous phenomena occur.

Concluding remarks. The relativistic thermodynamical laws obtained here will be used for the further study of the energy-momentum tensor in polarized media. In particular it will be shown in the next paper that a material energy-momentum tensor for switched-off fields and a corresponding field energy-momentum tensor may be found from thermodynamical considerations.

APPENDIX I

The nonrelativistic Hamiltonian for a dipole system. The Darwin-Lagrangian for a system of charged point particles ki (grouped into atoms, or other entities, numbered by k; the index $j = 1, 2, ..., f$ labels the constituent

particles) with charges e_{ki}, positions $\boldsymbol{R}_{ki}$ and velocities $\dot{\boldsymbol{R}}_{ki}$ which move in an external field with scalar and vector potentials $\varphi^{(e)}$ and $\boldsymbol{A}^{(e)}$, reads

$$L = \sum_{ki} \tfrac{1}{2} m_{ki} \dot{\boldsymbol{R}}_{ki}^2 + \sum_{ki} \frac{1}{8c^2} m_{ki} \dot{\boldsymbol{R}}_{ki}^4 - \sum_{k} \sum_{i,j=1,i\neq j}^{f} \frac{e_{ki} e_{kj}}{8\pi |\boldsymbol{R}_{ki} - \boldsymbol{R}_{kj}|}$$

$$\left\{ 1 - \frac{1}{2c^2} \dot{\boldsymbol{R}}_{ki} \cdot \mathbf{T}(\boldsymbol{R}_{ki}, \boldsymbol{R}_{kj}) \cdot \dot{\boldsymbol{R}}_{kj} \right\} - \sum_{k,l,k\neq l} \sum_{i,j=1}^{f} \frac{e_{ki} e_{lj}}{8\pi |\boldsymbol{R}_{ki} - \boldsymbol{R}_{lj}|}$$

$$\left\{ 1 - \frac{1}{2c^2} \dot{\boldsymbol{R}}_{ki} \cdot \mathbf{T}(\boldsymbol{R}_{ki}, \boldsymbol{R}_{lj}) \cdot \dot{\boldsymbol{R}}_{lj} \right\} - \sum_{ki} e_{ki} \left\{ \varphi^{(e)}(\boldsymbol{R}_{ki}) - \frac{\dot{\boldsymbol{R}}_{ki}}{c} \cdot \boldsymbol{A}^{(e)} (\boldsymbol{R}_{ki}) \right\}, \quad \text{(A 1)}$$

where, with $\boldsymbol{a}$ and $\boldsymbol{b}$ arbitrary vectors,

$$\mathbf{T}(\boldsymbol{a}, \boldsymbol{b}) = \mathbf{U} + \frac{(\boldsymbol{a} - \boldsymbol{b})(\boldsymbol{a} - \boldsymbol{b})}{|\boldsymbol{a} - \boldsymbol{b}|^2}. \quad \text{(A 2)}$$

If the last two terms of L are expanded in powers of $\boldsymbol{r}_{ki} = \boldsymbol{R}_{ki} - \boldsymbol{R}_k$, where $\boldsymbol{R}_k$ is the centre of gravity $\sum_{i=1}^{f} m_{ki} \boldsymbol{R}_{ki} / \sum_{i=1}^{f} m_{ki}$ of atom k, one obtains up to second order in $\boldsymbol{r}_{ki}$ (but discarding electric quadrupole moments $\tfrac{1}{2} \sum_{i=1}^{f} m_{ki} \boldsymbol{r}_{ki} \boldsymbol{r}_{ki}$) and up to zeroth order in c^{-1}:

$$L = \sum_{ki} \tfrac{1}{2} m_{ki} \dot{\boldsymbol{R}}_{ki}^2 - \tfrac{1}{2} \sum_{k} \sum_{i,j,i\neq j}^{f} \frac{e_{ki} e_{kj}}{4\pi |\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|}$$

$$- \tfrac{1}{2} \sum_{k,l,k\neq l} \boldsymbol{\mu}_k \cdot \boldsymbol{\nabla}_{R_k} \boldsymbol{\mu}_l \cdot \boldsymbol{\nabla}_{R_l} \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|}$$

$$- \tfrac{1}{2} \sum_{k,l,k\neq l} \boldsymbol{\nu}_k \cdot \boldsymbol{\nabla}_{R_k} \boldsymbol{\nu}_l \cdot \boldsymbol{\nabla}_{R_l} \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|}$$

$$+ \sum_{k} \boldsymbol{\mu}_k \cdot \boldsymbol{E}^{(e)}(\boldsymbol{R}_k) + \sum_{k} \boldsymbol{\nu}_k \cdot \boldsymbol{B}^{(e)}(\boldsymbol{R}_k), \quad \text{(A 3)}$$

where $\boldsymbol{\mu}_k = \sum_i e_{ki} \boldsymbol{r}_{ki}$ and $\boldsymbol{\nu}_k = \tfrac{1}{2} \sum_i e_{ki} \boldsymbol{r}_{ki} \wedge \dot{\boldsymbol{r}}_{ki}/c$ are the electric and magnetic dipole moments (the atoms carry no nett charge) and where $\boldsymbol{E}^{(e)}$ and $\boldsymbol{B}^{(e)}$ are the external electric and magnetic fields. This Lagrangian contains only terms of order c^0, if the c^{-1} in the magnetic dipole moment $\boldsymbol{\nu}_k$ is not taken into account; the magnetic dipole moment is considered as a characteristic atomic parameter on a par with the electric dipole moment.

Instead of the dependent position coordinates $\boldsymbol{R}_k$ and $\boldsymbol{r}_{ki}$, independent generalized $\boldsymbol{q}_{kj}$ are now introduced by means of

$$\boldsymbol{q}_{k1} = \boldsymbol{R}_k, \quad \boldsymbol{q}_{ki} = \boldsymbol{r}_{ki} \quad (i = 2, 3, \dots f). \quad \text{(A 4)}$$

Inversion gives with the help of $\sum_{i=1}^{f} m_{ki} \boldsymbol{r}_{ki} = 0$:

$$\boldsymbol{R}_k = \boldsymbol{q}_{k1}, \quad \boldsymbol{r}_{ki} = \boldsymbol{q}_{ki} - \delta_{i1} \sum_{j=1}^{f} \frac{m_{kj}}{m_{k1}} \boldsymbol{q}_{kj} \quad (i = 1, 2, \dots f). \quad \text{(A 5)}$$

The kinetic term in L becomes with $\boldsymbol{R}_{ki} = \boldsymbol{R}_k + \boldsymbol{r}_{ki}$ and (A 5):

$$K \equiv \sum_k \sum_{i=1}^f \tfrac{1}{2} m_{ki}\,\dot{\boldsymbol{R}}_{ki}^2 = \sum_k \tfrac{1}{2} m_k \dot{\boldsymbol{q}}_{k1}^2 +$$

$$+ \sum_k \sum_{i,j=2}^f \tfrac{1}{2}\left(m_{ki}\delta_{ij} + \frac{m_{ki}m_{kj}}{m_{k1}} \right) \dot{\boldsymbol{q}}_{ki}\cdot\dot{\boldsymbol{q}}_{kj}, \quad (A\ 6)$$

where $m_k = \sum_{i=1}^f m_{ki}$. Furthermore the dipole moments become with (A 5)

$$\boldsymbol{\mu}_k = -e_{k1}\sum_{i=2}^f \frac{m_{ki}}{m_{k1}}\,\boldsymbol{q}_{ki} + \sum_{i=2}^f e_{ki}\boldsymbol{q}_{ki}, \quad (A\ 7)$$

$$\boldsymbol{\nu}_k = \frac{1}{2c}\,e_{k1}\left(\sum_{i=2}^f \frac{m_{ki}}{m_{k1}}\,\boldsymbol{q}_{ki} \right)\wedge\left(\sum_{i=2}^f \frac{m_{ki}}{m_{k1}}\,\dot{\boldsymbol{q}}_{ki} \right) + \frac{1}{2c}\sum_{i=2}^f e_{ki}\boldsymbol{q}_{ki}\wedge\dot{\boldsymbol{q}}_{ki}. \quad (A\ 8)$$

With the help of (A 5–8) the Lagrangian (A 3) is found as a function of $\boldsymbol{q}_{ki}$ and $\dot{\boldsymbol{q}}_{ki}$. With the use of the canonical momenta $\boldsymbol{p}_{ki} \equiv \partial L/\partial\dot{\boldsymbol{q}}_{ki}$ one finds the function

$$H(\boldsymbol{q}, \dot{\boldsymbol{q}}) \equiv \sum_{ki} \boldsymbol{p}_{ki}\cdot\dot{\boldsymbol{q}}_{ki} - L =$$

$$= \tfrac{1}{2}\sum_k m_k\dot{\boldsymbol{q}}_{k1}^2 + \tfrac{1}{2}\sum_k \sum_{i,j=2}^f \left(m_{ki}\delta_{ij} + \frac{m_{ki}m_{kj}}{m_{k1}} \right) \dot{\boldsymbol{q}}_{ki}\cdot\dot{\boldsymbol{q}}_{kj}$$

$$+ \tfrac{1}{2}\sum_k \sum_{i,j,i\neq j} \frac{e_{ki}e_{kj}}{4\pi|\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|} + \tfrac{1}{2}\sum_{k,l,k\neq l} \boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_{q_{k1}}\boldsymbol{\mu}_l\cdot\boldsymbol{\nabla}_{q_{l1}} \frac{1}{4\pi|\boldsymbol{q}_{k1} - \boldsymbol{q}_{l1}|}$$

$$- \tfrac{1}{2}\sum_{k,l,k\neq l} \boldsymbol{\nu}_k\cdot\boldsymbol{\nabla}_{q_{k1}}\boldsymbol{\nu}_l\cdot\boldsymbol{\nabla}_{q_{l1}} \frac{1}{4\pi|\boldsymbol{q}_{k1} - \boldsymbol{q}_{l1}|} - \sum_k \boldsymbol{\mu}_k\cdot\boldsymbol{E}^{(e)}(\boldsymbol{q}_{k1}). \quad (A\ 9)$$

If the $\dot{\boldsymbol{q}}_{ki}$ are expressed in the canonical coordinates one gets for (A 9), neglecting terms of order c^{-2}, the Hamiltonian function

$$H(\boldsymbol{q}, \boldsymbol{p}) = \sum_k \frac{1}{2m_k}\boldsymbol{p}_{k1}^2 + \sum_k \left(\sum_{i=2}^f \frac{1}{2m_{ki}}\boldsymbol{p}_{ki}^2 - \frac{1}{2m_k}\sum_{i,j=2}^f \boldsymbol{p}_{ki}\cdot\boldsymbol{p}_{kj} \right)$$

$$+ \tfrac{1}{2}\sum_k \sum_{i,j,i\neq j} \frac{e_{ki}e_{kj}}{4\pi|\boldsymbol{r}_{ki} - \boldsymbol{r}_{kj}|} + \tfrac{1}{2}\sum_{k,l,k\neq l} \boldsymbol{\mu}_k\cdot\boldsymbol{\nabla}_{q_{k1}}\boldsymbol{\mu}_l\cdot\boldsymbol{\nabla}_{q_{l1}} \frac{1}{4\pi|\boldsymbol{q}_{k1} - \boldsymbol{q}_{l1}|}$$

$$+ \tfrac{1}{2}\sum_{k,l,k\neq l} \boldsymbol{\nu}_k\cdot\boldsymbol{\nabla}_{q_{k1}}\boldsymbol{\nu}_l\cdot\boldsymbol{\nabla}_{q_{l1}} \frac{1}{4\pi|\boldsymbol{q}_{k1} - \boldsymbol{q}_{l1}|} - \sum_k \boldsymbol{\mu}_k\cdot\boldsymbol{E}^{(e)}(\boldsymbol{q}_{k1}) - \sum_k \boldsymbol{\nu}_k\cdot\boldsymbol{B}^{(e)}(\boldsymbol{q}_{k1}).$$

$$(A\ 10)$$

This expression – in contrast with (A 9) – is symmetric in the electric and magnetic dipole moments $\boldsymbol{\mu}_k$ and $\boldsymbol{\nu}_k$.

APPENDIX II

The pressure tensor in an anisotropic medium. In order to prove the equality of the right-hand sides of (36) and (37) we start with the virial theorem

$$\left\langle \sum_{ki} \frac{d}{dt} (q_{ki} p_{ki}) \right\rangle = 0 \tag{A 11}$$

for equilibrium. We write this first as

$$\left\langle \sum_{k} \frac{d}{dt} (q_{k1} p_{k1}) \right\rangle + \left\langle \sum_{k, i, i \neq 1} \frac{d}{dt} (q_{ki} p_{ki}) \right\rangle = 0. \tag{A 12}$$

The second term contains the internal coordinates q_{ki} (v. (A 4)) and their canonically conjugate momenta p_{ki}. Therefore it vanishes in the adiabatic approximation[5]), according to which the atoms are in a pure state as far as internal coordinates are concerned*). The first term may be transformed with the use of Hamilton's equations, so that (A 12) becomes

$$\left\langle \sum_{k} \left(\frac{\partial H}{\partial p_{k1}} p_{k1} - q_{k1} \frac{\partial H}{\partial q_{k1}} \right) \right\rangle + \int \langle \sum_{k} q_{k1} f_{k1} \delta(R - q_{k1}) \rangle \, d\Omega = 0, \tag{A 13}$$

where H is the Hamilton function of the system and where $f_{k1} \delta(R - q_{k1}) \, d\Omega$ is the force exerted on atom k by an element of the wall $d\Omega$ situated at R. Now with the notation $\bar{f}(R)$ for the average force (per unit surface) exerted by the wall on the system, (A 13) becomes

$$\left\langle \sum_{k} \left(\frac{\partial H}{\partial p_{k1}} p_{k1} - q_{k1} \frac{\partial H}{\partial q_{k1}} \right) \right\rangle + \int R \bar{f}(R) \, d\Omega = 0. \tag{A 14}$$

Let us choose the centre of the ellipsoidal cell as the origin of the coordinate system. Then for a uniform strain characterized by the tensor $\delta \epsilon$ the displacements δR at the position R as compared to the displacement δR_0 at the origin is given by

$$\delta R - \delta R_0 = R \cdot \delta \epsilon. \tag{A 15}$$

Since the macroscopic velocity of the cell as a whole had been taken as zero, we have $\delta R_0 = 0$, so that (A 15) becomes

$$\delta R = R \cdot \delta \epsilon. \tag{A 16}$$

With this relation the second term of (A 14) contracted with the tensor $\delta \epsilon$ becomes:

$$\delta \tilde{\epsilon} \cdot \int R \bar{f}(R) \, d\Omega = \int \delta R \cdot \bar{f}(R) \, d\Omega, \tag{A 17}$$

---

*) If the average is performed with the help of the canonical ensemble one arrives directly at (A 12) without the second term [6]).

which is the work exerted by the wall on the system. If the displacement is performed adiabatically and at constant external fields $\boldsymbol{E}^{(e)}$ and $\boldsymbol{B}^{(e)}$, the right-hand side becomes $\delta\langle H\rangle$, where $\langle H\rangle$ is the average Hamiltonian of the cell. Then (A 17) gets the form

$$\int \boldsymbol{R}\bar{f}(\boldsymbol{R})\,\mathrm{d}\Omega = \left(\frac{\partial\langle H\rangle}{\partial\boldsymbol{\epsilon}}\right)_{\boldsymbol{E}^{(e)},\,\boldsymbol{B}^{(e)},\,S}. \tag{A 18}$$

If this is substituted into (A 14) one gets the result

$$\left\langle \sum_k \left(\frac{\partial H}{\partial \boldsymbol{p}_{k1}}\,\boldsymbol{p}_{k1} - \boldsymbol{q}_{k1}\,\frac{\partial H}{\partial \boldsymbol{q}_{k1}}\right)\right\rangle + \left(\frac{\partial\langle H\rangle}{\partial\boldsymbol{\epsilon}}\right)_{\boldsymbol{E}^{(e)},\,\boldsymbol{B}^{(e)},\,S} = 0. \tag{A 19}$$

The coordinate $\boldsymbol{q}_{k1}$ is the position $\boldsymbol{R}_k$ (A.4); denoting similarly its canonically conjugated momentum $\boldsymbol{p}_{k1}$ by $\boldsymbol{P}_k$ we may write:

$$\left\langle \sum_k \left(\frac{\partial H}{\partial \boldsymbol{P}_k}\,\boldsymbol{P}_k - \boldsymbol{R}_k\,\frac{\partial H}{\partial \boldsymbol{R}_k}\right)\right\rangle + \left(\frac{\partial\langle H\rangle}{\partial\boldsymbol{\epsilon}}\right)_{\boldsymbol{E}^{(e)},\,\boldsymbol{B}^{(e)},\,S} = 0, \tag{A 20}$$

which is used in section 3.

<div align="center">APPENDIX III</div>

On some mathematical identities in connexion with the depolarization tensor. We shall prove in this appendix some relations involving the depolarization tensor $\mathbf{L}(\boldsymbol{\epsilon})$ and the tensor $\mathbf{K}(\boldsymbol{\epsilon})$, which have been defined as:

$$\mathbf{L}(\boldsymbol{\epsilon}) = -\int\limits^{V(\boldsymbol{\epsilon})} \boldsymbol{V}_s\boldsymbol{V}_s\,\frac{1}{4\pi s}\,\mathrm{d}\boldsymbol{s}, \tag{A 21}$$

$$\mathbf{K}(\boldsymbol{\epsilon}) = \int\limits^{V(\boldsymbol{\epsilon})} s\boldsymbol{V}_s\boldsymbol{V}_s\boldsymbol{V}_s\,\frac{1}{4\pi s}\,\mathrm{d}\boldsymbol{s}, \tag{A 22}$$

where the integration over $\boldsymbol{s}$ is extended over a volume $V(\boldsymbol{\epsilon})$ of ellipsoidal shape, specified by the deformation tensor $\boldsymbol{\epsilon}$ (the integrals depend on the dimensions of the volume only through its shape). The vector $\boldsymbol{s}$ measures the position with respect to the centre of the ellipsoidal volume.

First we want to prove the relation

$$\int\limits^{V(\boldsymbol{\epsilon})} \boldsymbol{V}_{R_1}\boldsymbol{V}_{R_2}\,\frac{1}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|}\,\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2 = V\mathbf{L}(\boldsymbol{\epsilon}), \tag{A 23}$$

which has been used in section 3. It is equivalent to the identity:

$$\mathscr{P}_{\boldsymbol{\epsilon}}\int\limits^{V(\boldsymbol{\epsilon})} \boldsymbol{V}_{R_1}\boldsymbol{V}_{R_2}\,\frac{1}{4\pi|\boldsymbol{R}_1 - \boldsymbol{R}_2|}\,\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2 = 0, \tag{A 24}$$

where the principal value sign $\mathscr{P}_{\epsilon}$ means that an infinitesimal ellipsoid of shape determined by ϵ and with centre R_1 is excluded from the integration over R_2. If scale transformations of the coordinates are performed in the left-hand side of eq. (A 24) such that the integration domain becomes a sphere and if subsequently a Taylor expansion of the integrand is carried out, it follows that it is sufficient to prove identities of the form:

$$\mathscr{P}\int^{V}(R_1 - R_2)^n V_{R_1}^{n+2} \frac{1}{4\pi|R_1 - R_2|}\, dR_1\, dR_2 = 0 \qquad (n = 0, 1, 2, \ldots), \quad \text{(A 25)}$$

where $(R_1 - R_2)^n$ denotes a polyad of rank n and $V_{R_1}^{n+2}$ a polyad of rank $n + 2$. The integrations have to be extended now over a spherical volume, with the exclusion of an infinitesimally small sphere around R_1 from the integration over R_2. The left-hand side of (A 25) is an invariant tensor of rank $2n + 2$, which is symmetrical in the first n and in the last $n + 2$ indices. Furthermore traces taken with respect to a pair from the last $n + 2$ indices vanish identically. Thus the invariant tensor of rank $2n + 2$ may be considered as an element of the direct product space of symmetric tensors of rank n and symmetric traceless tensors of rank $n + 2$. Now symmetric tensors of rank n form a reducible representation of the rotation group which contains irreducible representations of dimension $2n + 1$, $2n - 3$, …, whereas the symmetric traceless tensors of rank $n + 2$ form an irreducible representation of dimension $2n + 5$. The direct product contains theretore irreducible representations of dimensionality higher than 1 only. Since the left-hand side of (A 25) is an *invariant* tensor which belongs to the direct product space it must vanish identically, so that (A 25) is proved and hence (A 23).

In an analogous way one may prove the relation:

$$\int^{V(\epsilon)} R_1 V_{R_1} V_{R_1} V_{R_2} \frac{1}{4\pi|R_1 - R_2|}\, dR_1\, dR_2 = -\tfrac{1}{2} V K(\epsilon). \qquad \text{(A 26)}$$

Finally we shall prove an identity connecting the derivative of $L(\epsilon)$ and $K(\epsilon)$:

$$\frac{\partial}{\partial \epsilon}\{v^{-1}L(\epsilon)\} = -v^{-1}K(\epsilon), \qquad \text{(A 27)}$$

which has been used in § 3 (formula (52)). Since $\partial v/\partial \epsilon$ is equal to vU, the left hand side of this identity may be written as:

$$v^{-1}\frac{\partial}{\partial \epsilon}L(\epsilon) - v^{-1}UL(\epsilon). \qquad \text{(A 28)}$$

According to the definition (A 21) of $L(\epsilon)$ one has for the variation due to

a deformation $\delta\epsilon$:

$$\delta\epsilon : \frac{\partial}{\partial\tilde{\epsilon}} \, \mathbf{L}(\epsilon) = - \int^{S(\epsilon)} \mathbf{n} \cdot \delta s \boldsymbol{V}_s \boldsymbol{V}_s \frac{1}{4\pi s} \, \mathrm{d}S, \tag{A 29}$$

where $\mathrm{d}S$ is a surface element (with normal unit vector $\mathbf{n}$) of the surface $S(\epsilon)$, which encloses the ellipsoidal volume $V(\epsilon)$. Furthermore δs is the deformation at the surface which is given by:

$$\delta s = s \cdot \delta\epsilon, \tag{A 30}$$

so that (A 29) gives

$$\frac{\partial}{\partial\tilde{\epsilon}} \, \mathbf{L}(\epsilon) = - \int^{V(\epsilon)} \boldsymbol{V}_s \left(s \boldsymbol{V}_s \boldsymbol{V}_s \frac{1}{4\pi s} \right) \mathrm{d}s. \tag{A 31}$$

If this is substituted in (A 28) one obtains after a differentiation in the integrand:

$$-v^{-1} \int^{V(\epsilon)} s \boldsymbol{V}_s \boldsymbol{V}_s \boldsymbol{V}_s \frac{1}{4\pi s} \, \mathrm{d}s; \tag{A 32}$$

according to (A 22) this expression is equal to the right-hand side of (A 27), which completes the proof.

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