CHAPTER X

Semi-relativistic quantum statistics of spin media

1 Introduction

By means of a quantum-statistical averaging procedure with Wigner functions the semi-relativistic macroscopic laws for spin media will be obtained in this chapter, on the basis of the microscopic results found in the preceding. This will lead to laws from which one may infer – by comparison with the non-relativistic results of chapter VII – which new terms arise if the spin of the particles is taken into account. At the end of the chapter the magnetostriction phenomenon will be studied on the basis of a simple model of a magnetic medium.

2 The Wigner function in statistics; particles with spin

In quantum-statistical mechanics the average value of a dynamical quantity, represented by an operator[1] A, is usually written as

$$\bar{A}(t) = \mathrm{Tr}\,\{P(t)A\}, \tag{1}$$

where $P(t)$ is the density operator

$$P(t) = \sum_{\gamma} w_\gamma |\psi(t)\rangle\langle\psi(t)| \tag{2}$$

that describes the macroscopic mixed state. The states $|\psi_\gamma(t)\rangle$, which form a complete orthonormal set, are weighted by the numbers w_γ, which are normalized to unity ($\sum_\gamma w_\gamma = 1$).

The average (1) of the operator A may be written in a different form, if one introduces Weyl transforms. As in section 3*c* of chapter VIII we denote the Weyl transform of the operator A by the symbol $a_{\kappa_1\ldots\kappa_N\lambda_1\ldots\lambda_N}(1, \ldots, N)$ depending on indices κ_i and λ_i ($i = 1, \ldots, N$), which in the present semi-relativistic description of systems of spin particles take the values 1 and 2.

[1] In this section capitals denote operators, lower case symbols their Weyl transforms.

The arguments 1, ..., N stand for the momentum and coordinate variables in a phase space of dimensionality 6^N for an N-particle system. The Wigner function is, apart from a factor h^{-3N}, equal to the Weyl transform of the density operator (2), so that it may be written as

$$\rho_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(1, \ldots, N; t) = \sum_\gamma w_\gamma \rho_{\gamma, \kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(1, \ldots, N; t) \qquad (3)$$

with partial Wigner functions ρ_γ given by (cf. (VI.A166)):

$$\rho_{\gamma, \kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(1, \ldots, N; t) \equiv \rho_{\gamma, \kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(\boldsymbol{p}_1, \boldsymbol{q}_1, \ldots, \boldsymbol{p}_N, \boldsymbol{q}_N; t)$$
$$= h^{-3N} \int \mathrm{d}\boldsymbol{v}_1 \ldots \mathrm{d}\boldsymbol{v}_N \exp\left(\frac{i}{\hbar} \sum_{i=1}^N \boldsymbol{p}_i \cdot \boldsymbol{v}_i\right) \psi_{\gamma, \kappa_1 \ldots \kappa_N}(\boldsymbol{q}_1 - \tfrac{1}{2}\boldsymbol{v}_1, \ldots, \boldsymbol{q}_N - \tfrac{1}{2}\boldsymbol{v}_N; t)$$
$$\psi^*_{\gamma, \lambda_1 \ldots \lambda_N}(\boldsymbol{q}_1 + \tfrac{1}{2}\boldsymbol{v}_1, \ldots, \boldsymbol{q}_N + \tfrac{1}{2}\boldsymbol{v}_N; t). \qquad (4)$$

In terms of this Wigner function one may write the average (1) as (cf. VI.A167)

$$\bar{A}(t) = \bar{a}(t) \equiv \sum_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N} \int \mathrm{d}1 \ldots \mathrm{d}N \, \rho_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(1, \ldots, N; t)$$
$$a_{\lambda_1 \ldots \lambda_N \kappa_1 \ldots \kappa_N}(1, \ldots, N). \qquad (5)$$

The right-hand side contains a trace over the matrix indices, which will be denoted by the symbol Sp (to distinguish it from the trace Tr in Hilbert space which is meant in (1)). Thus (5) may be written in the form

$$\bar{A}(t) = \bar{a}(t) \equiv \mathrm{Sp} \int \mathrm{d}1 \ldots \mathrm{d}N \, \rho(1, \ldots, N; t) a(1, \ldots, N). \qquad (6)$$

The Wigner function is normalized

$$\mathrm{Sp} \int \mathrm{d}1 \ldots \mathrm{d}N \, \rho(1, \ldots, N; t) = 1; \qquad (7)$$

as a result of the normalization $\sum_\gamma w_\gamma = 1$ (or Tr $P = 1$).

The time evolution of the Wigner function is governed by an equation of which (VI.A169) is the special case valid for a single particle in a pure state. It reads

$$\frac{\partial \rho_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(1, \ldots, N; t)}{\partial t} = \frac{1}{\hbar} \sin \left\{ \frac{\hbar}{2} \sum_{i=1}^N \left(\frac{\partial^{(h)}}{\partial \boldsymbol{q}^i} \cdot \frac{\partial^{(\rho)}}{\partial \boldsymbol{p}^i} - \frac{\partial^{(h)}}{\partial \boldsymbol{p}^i} \cdot \frac{\partial^{(\rho)}}{\partial \boldsymbol{q}^i} \right) \right\}$$
$$\sum_{\mu_1 \ldots \mu_N} (h_{\kappa_1 \ldots \kappa_N \mu_1 \ldots \mu_N} \rho_{\mu_1 \ldots \mu_N \lambda_1 \ldots \lambda_N} + \rho_{\kappa_1 \ldots \kappa_N \mu_1 \ldots \mu_N} h_{\mu_1 \ldots \mu_N \lambda_1 \ldots \lambda_N})$$
$$- \frac{i}{\hbar} \cos \left\{ \frac{\hbar}{2} \sum_{i=1}^N \left(\frac{\partial^{(h)}}{\partial \boldsymbol{q}^i} \cdot \frac{\partial^{(\rho)}}{\partial \boldsymbol{p}^i} - \frac{\partial^{(h)}}{\partial \boldsymbol{p}^i} \cdot \frac{\partial^{(\rho)}}{\partial \boldsymbol{q}^i} \right) \right\}$$
$$\sum_{\mu_1 \ldots \mu_N} (h_{\kappa_1 \ldots \kappa_N \mu_1 \ldots \mu_N} \rho_{\mu_1 \ldots \mu_N \lambda_1 \ldots \lambda_N} - \rho_{\kappa_1 \ldots \kappa_N \mu_1 \ldots \mu_N} h_{\mu_1 \ldots \mu_N \lambda_1 \ldots \lambda_N}), \qquad (8)$$

where the Weyl transform $h_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}$ of the Hamiltonian depends on the coordinates and momenta of all particles (i.e. on 1, ..., N), while the Wigner function $\rho_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}$ depends moreover on the time t.

As a consequence of the time behaviour (8) of the Wigner function the time derivative of the expectation value (6) of an operator is given by (cf. (VI.A170))

$$\frac{\mathrm{d}\bar{a}(t)}{\mathrm{d}t} = \frac{1}{\hbar} \mathrm{Sp} \int \mathrm{d}1 \ldots \mathrm{d}N \rho \left[\sin \left\{ \frac{\hbar}{2} \sum_{i=1}^N \left(\frac{\partial^{(a)}}{\partial \boldsymbol{q}_i} \cdot \frac{\partial^{(h)}}{\partial \boldsymbol{p}_i} - \frac{\partial^{(a)}}{\partial \boldsymbol{p}_i} \cdot \frac{\partial^{(h)}}{\partial \boldsymbol{q}_i} \right) \right\} (ah + ha) \right.$$
$$\left. - i \cos \left\{ \frac{\hbar}{2} \sum_{i=1}^N \left(\frac{\partial^{(a)}}{\partial \boldsymbol{q}_i} \cdot \frac{\partial^{(h)}}{\partial \boldsymbol{p}_i} - \frac{\partial^{(a)}}{\partial \boldsymbol{p}_i} \cdot \frac{\partial^{(h)}}{\partial \boldsymbol{q}_i} \right) \right\} (ah - ha) \right], \qquad (9)$$

where $a_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}$ and $h_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}$ depend on all coordinates and momenta (1, ..., N) and $\rho_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}$ moreover on the time t.

In the following it will be convenient to employ reduced Wigner functions, which are generalizations of the reduced Wigner functions for spinless particles.

The average of a sum of one-point functions (i.e. of quantities that depend on the coordinates and momenta of a single particle)

$$A \rightleftarrows a_{\kappa_1 \ldots \kappa_N \lambda_1 \ldots \lambda_N}(1, \ldots, N) = \sum_{i=1}^N \prod_{j(\neq i)} \delta_{\kappa_j \lambda_j} a_{i, \kappa_i \lambda_i}(i) \qquad (10)$$

may be written as

$$\bar{A}(t) = \mathrm{Sp} \int a_1(1) f_1(1; t) \mathrm{d}1 \qquad (11)$$

with the one-point reduced Wigner function defined as

$$f_{1, \kappa\lambda}(1; t) = N \sum_{\kappa_2 \ldots \kappa_N} \int \rho_{\kappa\kappa_2 \ldots \kappa_N \lambda\kappa_2 \ldots \kappa_N}(1, 2, \ldots, N) \mathrm{d}2 \ldots \mathrm{d}N, \qquad (12)$$

normalized to N.

In the same fashion one may employ two-point reduced Wigner functions

$$f_{2, \kappa_1\lambda_1\kappa_2\lambda_2}(1, 2; t) = N(N-1) \sum_{\kappa_3 \ldots \kappa_N} \int \rho_{\kappa_1\kappa_2 \ldots \kappa_N \lambda_1\lambda_2\kappa_3 \ldots \kappa_N}(1, 2, \ldots, N) \mathrm{d}3 \ldots \mathrm{d}N, \qquad (13)$$

normalized to $N(N-1)$, to write the average of a two-point function in a compact way.

The two-point correlation function is defined as

$$c_{2,\kappa_1\kappa_2\lambda_1\lambda_2}(1,2;t) = f_{2,\kappa_1\kappa_2\lambda_1\lambda_2}(1,2;t) - f_{1,\kappa_1\lambda_1}(1;t) f_{1,\kappa_2\lambda_2}(2;t), \qquad (14)$$

normalized to $-N$.

3 The Maxwell equations

The macroscopic field equations will follow from the atomic equations of chapter IX, section 5. Let us multiply these equations, valid for Weyl transforms, with a Wigner function, integrate over all coordinates and momenta, and take the spur. The resulting equations are still not in the form of the Maxwell equations, since they contain terms as $\overline{\partial_{0P}\boldsymbol{p}}$ instead of $\partial_0\overline{\boldsymbol{p}}$, where $\boldsymbol{p}$ is the Weyl transform of the atomic polarization (and likewise two terms with the electric and magnetic fields). However they may be brought into the desired form, if one employs the identity (9) for the polarization density and the fields. Let us consider first the time derivative $\partial_0 \boldsymbol{p}$. With the help of the expressions (IX.63) with (IX.64–65) for the Weyl transform of the polarization and (IX.37) for the Weyl transform of the Hamiltonian of the system we find that in the right-hand side of (9) the cosine term does not contribute, while the sine term reduces to the average of the Poisson bracket $\overline{\partial_{0P}\boldsymbol{p}}$. This shows that indeed $\overline{\partial_{0P}\boldsymbol{p}}$ may be replaced by $\partial_0\overline{\boldsymbol{p}}$.

The derivatives of the electromagnetic fields may be treated along similar lines by using the Weyl transforms of the atomic fields (v. (IX.46)). Then again one proves that $\overline{\partial_{0P}\boldsymbol{e}}$ and $\overline{\partial_{0P}\boldsymbol{b}}$ are equal to $\partial_0\overline{\boldsymbol{e}}$ and $\partial_0\overline{\boldsymbol{b}}$. If one writes $\boldsymbol{E}, \boldsymbol{B}, \varrho^e, \boldsymbol{J}, \boldsymbol{P}$, and $\boldsymbol{M}$ for the averages $\overline{\boldsymbol{e}}, \overline{\boldsymbol{b}}, \overline{\rho^e}, \overline{\boldsymbol{j}}, \overline{\boldsymbol{p}}$ and $\overline{\boldsymbol{m}}$ of the corresponding atomic quantities one recovers indeed the Maxwell equations:

$$\begin{aligned} \nabla\cdot\boldsymbol{E} &= \varrho^e - \nabla\cdot\boldsymbol{P}, \\ -\partial_0\boldsymbol{E} + \nabla\wedge\boldsymbol{B} &= c^{-1}\boldsymbol{J} + \partial_0\boldsymbol{P} + \nabla\wedge\boldsymbol{M}, \\ \nabla\cdot\boldsymbol{B} &= 0, \\ \partial_0\boldsymbol{B} + \nabla\wedge\boldsymbol{E} &= 0. \end{aligned} \qquad (15)$$

The sources ϱ^e, $\boldsymbol{J}$, $\boldsymbol{P}$ and $\boldsymbol{M}$ are again found as statistical averages of (IX.58) and (IX.63) and thus ultimately expressed in terms of the atomic charges e_k and electromagnetic multipole moments $\boldsymbol{\mu}_k^{(n)}$ and $\boldsymbol{\nu}_k^{(n)}$. They contain the complete semi-relativistic contributions due to the spins of the constituent electrons of the atoms.

4 The momentum and energy equations

a. *Conservation of rest mass*

The atomic rest mass density is given by its Weyl transform

$$\rho \equiv \sum_k m_k \delta(\boldsymbol{X}_k - \boldsymbol{R}) \qquad (16)$$

with $\boldsymbol{X}_k$ the Weyl transform (IX.68) of the position operator for the atom as a whole. The definition of the delta function is analogous to that of (IX.52). The quantity m_k is the total rest mass $\sum_i m_{ki}$ of the atom. The Weyl transform ρ satisfies the conservation law

$$\partial_{tP}\rho = -\nabla\cdot\{\sum_k m_k \boldsymbol{v}_k \delta(\boldsymbol{X}_k - \boldsymbol{R})\} \qquad (17)$$

with $\boldsymbol{v}_k \equiv \partial_{tP}\boldsymbol{X}_k$ and $\partial_{tP}\rho$ the Poisson bracket of the density ρ and the Weyl transform of the Hamiltonian. We used the fact that $\boldsymbol{v}_k$ commutes with $\boldsymbol{X}_k$ in semi-relativistic approximation, since the non-diagonal matrix part of $\boldsymbol{X}_k$ is of order c^{-2} while the part of order c^0 in $\boldsymbol{v}_k$ is diagonal.

A macroscopic conservation law is obtained from (17) by multiplying it by a Wigner function, integrating over phase space and taking the spur of the matrices. Then one obtains for the left-hand side of (17) the expression $\overline{\partial_{tP}\rho}$, which may be shown to be equal to $\partial_t\overline{\rho}$. Indeed one may conclude this from (9) by inspection of the expressions (16) for ρ and (IX.37) for the Weyl transform of the Hamiltonian, if one confines oneself to semi-relativistic terms. Thus the macroscopic conservation law of rest mass gets the usual form

$$\frac{\partial\varrho}{\partial t} = -\nabla\cdot(\varrho\boldsymbol{v}), \qquad (18)$$

where the mass density and the mass flow density are given by

$$\varrho = \overline{\rho} = \mathrm{Sp}\int m_1 \delta(\boldsymbol{X}_1 - \boldsymbol{R}) f_1(1;t)\mathrm{d}1, \qquad (19)$$

$$\varrho\boldsymbol{v} = \mathrm{Sp}\int m_1 \boldsymbol{v}_1 \delta(\boldsymbol{X}_1 - \boldsymbol{R}) f_1(1;t)\mathrm{d}1. \qquad (20)$$

Here we introduced the one-point reduced Wigner functions (12). The expressions (19) with (20) serve to define the macroscopic velocity $\boldsymbol{v}(\boldsymbol{R}, t)$.

b. *The momentum balance*

The momentum law will follow by multiplying the atomic law (IX.75) by

$\delta(\boldsymbol{X}_k-\boldsymbol{R})$, summing over k and averaging with a Wigner function. The left-hand side may be written as

$$\operatorname{Sp}\int \sum_k \partial_{t\mathrm{P}}\{(m_k \boldsymbol{v}_k+\boldsymbol{g}_k)\delta(\boldsymbol{X}_k-\boldsymbol{R})\}\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N$$
$$+\nabla\cdot\operatorname{Sp}\int \sum_k \boldsymbol{v}_k(m_k \boldsymbol{v}_k+\boldsymbol{g}_k)\delta(\boldsymbol{X}_k-\boldsymbol{R})\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N, \qquad (21)$$

where we used the fact that in the semi-relativistic approximation $\boldsymbol{v}_k$ commutes with the expression between the brackets, because both $\boldsymbol{v}_k$ and $\boldsymbol{X}_k$ are of the form of a diagonal matrix of order c^0 and c^{-1} plus a non-diagonal matrix of order c^{-2}.

In the first term of (21) we may apply formula (9) to write it as the time derivative of an average. Indeed it follows from the forms of $\boldsymbol{X}_k$ (IX.68), $\boldsymbol{g}_k$ (IX.69), $\boldsymbol{v}_k$ and the Weyl transform of the Hamilton operator (IX.37) that the sine and cosine terms occurring in (9) reduce to a Poisson bracket. Then this first term becomes $\partial(\varrho\boldsymbol{v}+\boldsymbol{g})/\partial t$ with

$$\boldsymbol{g} \equiv \operatorname{Sp}\int \boldsymbol{g}_1\,\delta(\boldsymbol{X}_1-\boldsymbol{R})f_1(1;t)\mathrm{d}1. \qquad (22)$$

In the second term of (21) the velocity $\boldsymbol{v}_k$ will be split into the macroscopic velocity at the position $\boldsymbol{R}$, defined by (20) with (19), and a fluctuation term:

$$\boldsymbol{v}_k = \boldsymbol{v}(\boldsymbol{R},t)+\hat{\boldsymbol{v}}_k(\boldsymbol{R},t). \qquad (23)$$

Then we may write this second term of (21) in the form

$$\nabla\cdot(\varrho\boldsymbol{v}\boldsymbol{v}+\boldsymbol{v}\boldsymbol{g}+\mathsf{P}^{\mathrm{K}}) \qquad (24)$$

with the kinetic pressure

$$\mathsf{P}^{\mathrm{K}} \equiv \operatorname{Sp}\int \hat{\boldsymbol{v}}_1(m_1\hat{\boldsymbol{v}}_1+\boldsymbol{g}_1)\delta(\boldsymbol{X}_1-\boldsymbol{R})f_1(1;t)\mathrm{d}1 \qquad (25)$$

and the momentum density $\boldsymbol{g}$ (22). Thus we have found that the momentum balance equation reads

$$\frac{\partial(\varrho\boldsymbol{v}+\boldsymbol{g})}{\partial t} = -\nabla\cdot(\varrho\boldsymbol{v}\boldsymbol{v}+\boldsymbol{v}\boldsymbol{g}+\mathsf{P}^{\mathrm{K}})+\boldsymbol{F}^{\mathrm{L}}+\boldsymbol{F}^{\mathrm{S}} \qquad (26)$$

with the long range and short range force densities:

$$\boldsymbol{F}^{\mathrm{L,S}} = \operatorname{Sp}\int \sum_k \boldsymbol{f}_k^{\mathrm{L,S}}\delta(\boldsymbol{X}_k-\boldsymbol{R})\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N. \qquad (27)$$

To specify the equation (26) completely, we shall now study the explicit expressions that result if (IX.71) with (IX.73) and (IX.74) are introduced into (27). The external field terms of the long range force density follow from (IX.71). We find, using the macroscopic charge–current and polarization densities ϱ^{e}, $\boldsymbol{J}$, $\boldsymbol{P}$ and $\boldsymbol{M}$ of section 3, and limiting ourselves to dipole substances, for these terms

$$\boldsymbol{F}_{\mathrm{e}}^{\mathrm{L}} = \varrho^{\mathrm{e}}\boldsymbol{E}_{\mathrm{e}}+c^{-1}\boldsymbol{J}\wedge\boldsymbol{B}_{\mathrm{e}}+(\nabla\boldsymbol{E}_{\mathrm{e}})\cdot\boldsymbol{P}+(\nabla\boldsymbol{B}_{\mathrm{e}})\cdot\boldsymbol{M}$$
$$+c^{-1}\operatorname{Sp}\int\sum_k \partial_{t\mathrm{P}}\{\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{B}_{\mathrm{e}}(\boldsymbol{X}_k,t)-\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge\boldsymbol{E}_{\mathrm{e}}(\boldsymbol{X}_k,t)\}\delta(\boldsymbol{X}_k-\boldsymbol{R})$$
$$\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N. \qquad (28)$$

The last term may be written as

$$c^{-1}\operatorname{Sp}\int\sum_k \partial_{t\mathrm{P}}[\{\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{B}_{\mathrm{e}}(\boldsymbol{X}_k,t)-\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge\boldsymbol{E}_{\mathrm{e}}(\boldsymbol{X}_k,t)\}\delta(\boldsymbol{X}_k-\boldsymbol{R})]$$
$$\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N$$
$$+c^{-1}\nabla\cdot\operatorname{Sp}\int\sum_k \boldsymbol{v}_k\{\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{B}_{\mathrm{e}}(\boldsymbol{X}_k,t)-\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge\boldsymbol{E}_{\mathrm{e}}(\boldsymbol{X}_k,t)\}\delta(\boldsymbol{X}_k-\boldsymbol{R})$$
$$\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N, \qquad (29)$$

since $c^{-1}\boldsymbol{v}_k$ commutes with $\boldsymbol{X}_k$ and with $\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{B}_{\mathrm{e}}-\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge\boldsymbol{E}_{\mathrm{e}}$ in semi-relativistic approximation. In the first term of (29) one applies the identity (9). By inspection of the integrand of (29) and the Weyl transform of the Hamiltonian (IX.37), it follows that the cosine term does not contribute and of the sine term only the Poisson bracket, so that one may write for (29)

$$c^{-1}\frac{\partial}{\partial t}(\boldsymbol{P}\wedge\boldsymbol{B}_{\mathrm{e}}-\boldsymbol{M}_{\mathrm{orb}}\wedge\boldsymbol{E}_{\mathrm{e}})+c^{-1}\nabla\cdot\{\boldsymbol{v}(\boldsymbol{P}\wedge\boldsymbol{B}_{\mathrm{e}}-\boldsymbol{M}_{\mathrm{orb}}\wedge\boldsymbol{E}_{\mathrm{e}})\}$$
$$+c^{-1}\nabla\cdot\operatorname{Sp}\int\sum_k \hat{\boldsymbol{v}}_k(\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{B}_{\mathrm{e}}-\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge\boldsymbol{E}_{\mathrm{e}})\delta(\boldsymbol{X}_k-\boldsymbol{R})$$
$$\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N, \qquad (30)$$

where the macroscopic orbital magnetic dipole density

$$\boldsymbol{M}_{\mathrm{orb}} \equiv \operatorname{Sp}\int \boldsymbol{v}_{1,\mathrm{orb}}^{(1)}\delta(\boldsymbol{X}_1-\boldsymbol{R})f_1(1;t)\mathrm{d}1 \qquad (31)$$

and the velocity fluctuation $\hat{\boldsymbol{v}}_k$ of (23) have been introduced.

The interatomic field contribution to the long range force density follows from (IX.73). It may be split into an uncorrelated and a correlated part, if one employs the definition of the two-point Wigner correlation function (14). One finds in this fashion for the sum of the interatomic and external field contributions i.e. for the total long range force density

$$F^{L} = \varrho^{e}E + c^{-1}J\wedge B + (\nabla E)\cdot P + (\nabla B)\cdot M + c^{-1}\frac{\partial}{\partial t}(P\wedge B - M_{orb}\wedge E)$$
$$+ c^{-1}\nabla\cdot\{v(P\wedge B - M_{orb}\wedge E)\} - \nabla\cdot\mathbf{P}^{F} + F^{C}, \quad (32)$$

where the Maxwell fields E and B appear. The field dependent part of the pressure is given by:

$$\mathbf{P}^{F} \equiv -c^{-1}\,\mathrm{Sp}\int \hat{v}_1(\mu_1^{(1)}\wedge B - \nu_{1,orb}^{(1)}\wedge E)\delta(X_1 - R)f_1(1;t)\mathrm{d}1 \quad (33)$$

and the correlation force density by

$$F^{C} = \mathrm{Sp}\int f^{C}(1,2)\delta(X_1 - R)c_2(1,2;t)\mathrm{d}1\,\mathrm{d}2, \quad (34)$$

where we introduced the abbreviation:

$$f^{C}(1,2) \equiv -\{\sum_{n,m=0}^{\infty}\mu_1^{(n)} : \nabla_1^{n}\,\mu_2^{(m)} : \nabla_2^{m}\nabla_1$$
$$+ \sum_{n,m=1}^{\infty}(\nabla_1^{n-1} : \nu_1^{(n)}\wedge\nabla_1)\cdot(\nabla_2^{m-1} : \nu_2^{(m)}\wedge\nabla_1)\nabla_1\}\frac{1}{4\pi|X_1 - X_2|}. \quad (35)$$

An expression for the short range force density F^{S} (27) in the momentum balance (26) follows if one inserts (IX.74):

$$F^{S} = \mathrm{Sp}\int f^{S}(1,2)\delta(X_1 - R)f_2(1,2;t)\mathrm{d}1\,\mathrm{d}2 \quad (36)$$

with the abbreviation

$$f^{S}(1,2) \equiv -\sum_{i,j}\Big[1 - c^{-2}(\partial_{tP}r_{1i})\cdot(\partial_{tP}r_{2j})$$
$$+ c^{-2}\{\partial_{tP}(r_{1i} - r_{2j})\}\cdot\left\{\left(\frac{\hbar}{2m_{1i}}\sigma_{1i} + \frac{\hbar}{2m_{2j}}\sigma_{2j}\right)\wedge\nabla_{1i}\right\}$$
$$+ c^{-2}\frac{\hbar^2}{4m_{1i}m_{2j}}(\sigma_{1i}\wedge\nabla_{1i})\cdot(\sigma_{2j}\wedge\nabla_{1i})\Big]\nabla_{1i}\frac{e_{1i}e_{2j}}{4\pi|X_{1i} - X_{2j}|} - f^{C}(1,2). \quad (37)$$

Owing to the antisymmetric character of (37) with respect to the interchange of 1 and 2, one may write (36) as

$$F^{S} = \tfrac{1}{2}\mathrm{Sp}\int f^{S}(1,2)\{\delta(X_1 - R) - \delta(X_2 - R)\}f_2(1,2;t)\mathrm{d}1\,\mathrm{d}2. \quad (38)$$

Then, since $f^{S}(1,2)$ diminishes rapidly with increasing interatomic distances we may apply an Irving–Kirkwood procedure to write (38) as a divergence[1]:

$$F^{S} = -\nabla\cdot\mathbf{P}^{S} \quad (39)$$

with the short range pressure

$$\mathbf{P}^{S} \equiv \tfrac{1}{2}\,\mathrm{Sp}\int(X_1 - X_2)f^{S}(1,2)\delta\{\tfrac{1}{2}(X_1 + X_2) - R\}f_2(1,2;t)\mathrm{d}1\,\mathrm{d}2. \quad (40)$$

We are left with the correlation force density F^{C} (34). For systems of neutral atoms in which no long range Wigner correlations exist, so that a correlation length may be defined, one may apply an Irving–Kirkwood procedure to the correlation terms as well. One gets then

$$F^{C} = -\nabla\cdot\mathbf{P}^{C} \quad (41)$$

with a correlation pressure given by

$$\mathbf{P}^{C} \equiv \tfrac{1}{2}\,\mathrm{Sp}\int(X_1 - X_2)f^{C}(1,2)\delta\{\tfrac{1}{2}(X_1 + X_2) - R\}c_2(1,2;t)\mathrm{d}1\,\mathrm{d}2. \quad (42)$$

Hence we have found now the macroscopic momentum balance equation

$$\frac{\partial(\varrho v + g)}{\partial t} = -\nabla\cdot(\varrho vv + vg + \mathbf{P}) + (\nabla E)\cdot P + (\nabla B)\cdot M$$
$$+ c^{-1}\frac{\partial}{\partial t}(P\wedge B - M_{orb}\wedge E) + c^{-1}\nabla\cdot\{v(P\wedge B - M_{orb}\wedge E)\} \quad (43)$$

with the total pressure tensor

$$\mathbf{P} = \mathbf{P}^{K} + \mathbf{P}^{F} + \mathbf{P}^{C} + \mathbf{P}^{S}, \quad (44)$$

valid for systems of neutral atoms without long range correlations. The Lorentz force density, which occurs in (32), is absent for systems with neutral atoms.

As compared with the non-relativistic theory, namely with (VII.64), the momentum density contains an additional term g specified in (22) with (IX.69). The pressure tensor includes, apart from a similar additional term in its kinetic part (25), additional terms due to the interaction of magnetic

[1] In contrast with the procedure used in earlier chapters, where the distribution functions were developed, we employ here the equivalent methods of developing the delta functions. This has a formal advantage because the delta functions have to be understood as (IX.52). Integration over R_1 would lead then to slightly more complicated expressions, which are now avoided.

dipoles with each other, as (40) and (42) with (35) and (37) show. In the terms that depend solely on the Maxwell fields $(\boldsymbol{E}, \boldsymbol{B})$, the polarization densities $(\boldsymbol{P}, \boldsymbol{M})$ and the macroscopic velocity $\boldsymbol{v}$ two extra terms appear, which couple the orbital magnetization density $\boldsymbol{M}_{\mathrm{orb}}$ to the electric field. These terms may be written in alternative form by using mass conservation, namely as

$$-c^{-1}\varrho \frac{\mathrm{d}}{\mathrm{d}t}\{v(\boldsymbol{M}_{\mathrm{orb}} \wedge \boldsymbol{E})\} \tag{45}$$

(with v the specific volume and $\mathrm{d}/\mathrm{d}t$ the material time derivative $\partial/\partial t + \boldsymbol{v}\cdot\nabla$): the magnetodynamic effect on the macroscopic level. It contains only the orbital part of the magnetization, since the spin magnetization is assumed to be completely normal (without an anomalous contribution). Furthermore the Maxwell fields and the polarization densities also contain terms due to the presence of spins.

By employing the Maxwell equations one may write the balance equation (43) in the form of a conservation law:

$$\begin{aligned}\frac{\partial}{\partial t}\{\varrho\boldsymbol{v}+\boldsymbol{g}+c^{-1}\boldsymbol{E}\wedge(\boldsymbol{B}-\boldsymbol{M}_{\mathrm{orb}})\}&\\ +\nabla\cdot\{\varrho\boldsymbol{v}\boldsymbol{v}+\boldsymbol{v}\boldsymbol{g}+\mathsf{P}-\boldsymbol{D}\boldsymbol{E}-\boldsymbol{B}\boldsymbol{H}-c^{-1}\boldsymbol{v}(\boldsymbol{P}\wedge\boldsymbol{B}-\boldsymbol{M}_{\mathrm{orb}}\wedge\boldsymbol{E})&\\ +(\tfrac{1}{2}E^2+\tfrac{1}{2}B^2-\boldsymbol{M}\cdot\boldsymbol{B})\mathsf{U}\} &= 0. \end{aligned}\tag{46}$$

The method outlined may be extended to plasmas and to systems with long range correlations. In the latter case one has to introduce a mean correlation function $\bar{c}_2(1, 2; t)$, as discussed for instance in chapter II, section 5*h*.

c. *The energy balance*

The energy balance equation on the macroscopic level will be derived from its atomic counterpart (IX.86). Multiplying the latter by $\delta(\boldsymbol{X}_k-\boldsymbol{R})$, summing over k and averaging with a Wigner function yield an equation of which the left-hand side may be written as:

$$\begin{aligned}&\mathrm{Sp}\int\sum_k \partial_{t\mathrm{P}}\{(\tfrac{1}{2}m_k\boldsymbol{v}_k^2+\boldsymbol{v}_k\cdot\boldsymbol{g}_k+t_k+u_k)\delta(\boldsymbol{X}_k-\boldsymbol{R})\}\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N\\ &\quad+\nabla\cdot\,\mathrm{Sp}\int\sum_k \boldsymbol{v}_k(\tfrac{1}{2}m_k\boldsymbol{v}_k^2+\boldsymbol{v}_k\cdot\boldsymbol{g}_k+t_k+u_k)\delta(\boldsymbol{X}_k-\boldsymbol{R})\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N.\end{aligned}\tag{47}$$

In the first term of this expression we apply the identity (9). In the present

case it leads to the following form

$$\begin{aligned}&\frac{\partial}{\partial t}\mathrm{Sp}\int\sum_k(\tfrac{1}{2}m_k\boldsymbol{v}_k^2+\boldsymbol{v}_k\cdot\boldsymbol{g}_k+t_k+u_k)\delta(\boldsymbol{X}_k-\boldsymbol{R})\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N\\ &\quad+\frac{\hbar^2}{24}\mathrm{Sp}\int\Bigg[\Bigg\{\sum_{l,j}3\frac{\partial}{\partial\boldsymbol{R}_{lj}}\cdot\frac{\partial^{(H)}}{\partial\boldsymbol{P}_{lj}}\Bigg(\sum_{m,p}\frac{\partial}{\partial\boldsymbol{P}_{mp}}\cdot\frac{\partial^{(H)}}{\partial\boldsymbol{R}_{mp}}\Bigg)^2-\Bigg(\sum_{l,j}\frac{\partial}{\partial\boldsymbol{P}_{lj}}\cdot\frac{\partial^{(H)}}{\partial\boldsymbol{R}_{lj}}\Bigg)^3\Bigg\}\\ &\quad\quad H(1,\ldots,N;t)\sum_k(\tfrac{1}{2}m_k\boldsymbol{v}_k^2+\boldsymbol{v}_k\cdot\boldsymbol{g}_k+t_k+u_k)\delta(\boldsymbol{X}_k-\boldsymbol{R})\Bigg]\\ &\qquad\qquad\qquad\qquad\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N,\end{aligned}\tag{48}$$

where $H(1, \ldots, N; t)$ is the Weyl transform of the Hamiltonian. The superscripts (H) at the differential operators indicate that they act only on the Hamiltonian, while the other operators act on all functions under the brackets save for the Hamiltonian. Using the explicit expression (IX.37) for $H(1, \ldots, N; t)$, one finds in the semi-relativistic approximation for the second term of (48) the divergence

$$\nabla\cdot\boldsymbol{J}_q^{\mathrm{K}'} \tag{49}$$

of the vector

$$\begin{aligned}\boldsymbol{J}_q^{\mathrm{K}'}\equiv{}&\mathrm{Sp}\int\frac{\hbar^2}{8}\sum_{k,i}\frac{e_{ki}}{m_k m_{ki}c}\{\Delta_{ki}\boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}_{ki},t)\}\delta(\boldsymbol{X}_k-\boldsymbol{R})\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N\\ &-\mathrm{Sp}\int\frac{\hbar^2}{16}\sum_k\sum_{i,j(i\neq j)}\frac{e_{ki}e_{kj}\hbar}{m_k m_{ki}c^2}\Big(\frac{1}{m_{ki}}+\frac{1}{m_{kj}}\Big)\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki}\delta(\boldsymbol{X}_{ki}-\boldsymbol{X}_{kj})\delta(\boldsymbol{X}_k-\boldsymbol{R})\\ &\qquad\qquad\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N\\ &+\mathrm{Sp}\int\frac{\hbar^2}{16}\sum_{k,l(k\neq l)}\sum_{i,j}\frac{e_{ki}e_{kj}\hbar}{m_k m_{ki}m_{lj}c^2}\boldsymbol{\sigma}_{lj}\wedge\nabla_{ki}\delta(\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj})\delta(\boldsymbol{X}_k-\boldsymbol{R})\\ &\qquad\qquad\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N.\end{aligned}\tag{50}$$

The first term with the vector potential of the external field has been found already in the non-relativistic treatment of chapter VII. It was shown there that such a term does not spoil the gauge invariance. The second term contains semi-relativistic contributions connected with the presence of spin. Collecting the results (47–50) we find the macroscopic energy balance in the form

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho\boldsymbol{v}^2+\boldsymbol{v}\cdot\boldsymbol{g}+\varrho u^{\mathrm{K}}) = -\nabla\cdot\{\boldsymbol{v}(\tfrac{1}{2}\varrho\boldsymbol{v}^2+\boldsymbol{v}\cdot\boldsymbol{g}+\varrho u^{\mathrm{K}})+\mathsf{P}^{\mathrm{K}}\cdot\boldsymbol{v}+\boldsymbol{J}_q^{\mathrm{K}}\}+\Psi^{\mathrm{L}}+\Psi^{\mathrm{S}}. \tag{51}$$

It contains a kinetic contribution to the energy density

$$\varrho u^{\mathrm{K}} \equiv \mathrm{Sp}\int(\tfrac{1}{2}m_1\hat{\boldsymbol{v}}_1^2+\hat{\boldsymbol{v}}_1\cdot\boldsymbol{g}_1+t_1+u_1)\delta(\boldsymbol{X}_1-\boldsymbol{R})f_1(1;t)\mathrm{d}1 \tag{52}$$

and a kinetic heat flow

$$J_q^{\mathrm{K}} \equiv \mathrm{Sp}\int \hat{v}_1(\tfrac{1}{2}m_1\hat{v}_1^2+\hat{v}_1\cdot g_1+t_1+u_1)\delta(X_1-R)f_1(1;t)\mathrm{d}1+J_q^{\mathrm{K}'}. \quad (53)$$

The long range and short range power densities Ψ^{L} and Ψ^{S} stand for the expressions

$$\Psi^{\mathrm{L,S}} \equiv \mathrm{Sp}\int \sum_k \psi_k^{\mathrm{L,S}}\delta(X_k-R)\rho(1,\ldots,N;t)\mathrm{d}1\ldots\mathrm{d}N. \quad (54)$$

The long range power density Ψ^{L} is found explicitly by considering first the external, then the interatomic field contributions (splitting the latter into an uncorrelated and a correlated part with the help of (14)) and using the identity (9). Then one finds in the present semi-relativistic case

$$\Psi^{\mathrm{L}} = J\cdot E+\frac{\partial P}{\partial t}\cdot E+\nabla\cdot(vP\cdot E)-M\cdot\frac{\partial B}{\partial t}+\frac{\partial}{\partial t}(M_{\mathrm{spin}}\cdot B)+\nabla\cdot(vM_{\mathrm{spin}}\cdot B)$$
$$+2c^{-1}\frac{\partial}{\partial t}\{v\cdot(E\wedge M_{\mathrm{orb}})\}+2c^{-1}\nabla\cdot\{vv\cdot(E\wedge M_{\mathrm{orb}})\}-\frac{\partial\varrho u^{\mathrm{F}}}{\partial t}$$
$$-\nabla\cdot(v\varrho u^{\mathrm{F}}+\mathsf{P}^{\mathrm{F}}\cdot v+J_q^{\mathrm{F}})+\Psi^{\mathrm{C}}. \quad (55)$$

Here the macroscopic fields E, B, the macroscopic current density J, the polarization densities P, $M = M_{\mathrm{orb}}+M_{\mathrm{spin}}$ appear and moreover – also separately – the macroscopic orbital and spin magnetic dipole densities M_{orb} (31) and

$$M_{\mathrm{spin}} = \mathrm{Sp}\int \nu_{1,\mathrm{spin}}^{(1)}\delta(X_1-R)f_1(1;t)\mathrm{d}1. \quad (56)$$

The symbol ϱu^{F} stands for that part of the energy density ϱu which depends explicitly on the Maxwell fields. It is defined as

$$\varrho u^{\mathrm{F}} = -2c^{-1}\left\{\int \nu_{1,\mathrm{orb}}^{(1)}\wedge\hat{v}_1\,\delta(X_1-R)f_1(1;t)\mathrm{d}1\right\}\cdot E. \quad (57)$$

The field dependent part P^{F} of the pressure tensor has been given in (33), while that of the heat flow is defined as

$$J_q^{\mathrm{F}} = -\left\{\mathrm{Sp}\int \hat{v}_1(\mu_1^{(1)}-c^{-1}\nu_1^{(1)}\wedge\hat{v}_1)\delta(X_1-R)f_1(1;t)\mathrm{d}1\right\}\cdot(E+c^{-1}v\wedge B)$$
$$-\left\{\mathrm{Sp}\int \hat{v}_1\,\nu_{1,\mathrm{spin}}^{(1)}\delta(X_1-R)f_1(1;t)\mathrm{d}1\right\}\cdot(B-c^{-1}v\wedge E)$$
$$-2c^{-1}\left\{\mathrm{Sp}\int \hat{v}_1\,\nu_{1,\mathrm{orb}}^{(1)}\wedge\hat{v}_1\,\delta(X_1-R)f_1(1;t)\mathrm{d}1\right\}\cdot E. \quad (58)$$

Finally the power density due to the correlations in the system is given by

$$\Psi^{\mathrm{C}} = \mathrm{Sp}\int \{\psi^{\mathrm{C}}(1,2)+v\cdot f^{\mathrm{C}}(1,2)\}\delta(X_1-R)c_2(1,2;t)\mathrm{d}1\,\mathrm{d}2, \quad (59)$$

where we employed the abbreviations f^{C} (35) and

$$\psi^{\mathrm{C}}(1,2) \equiv -\sum_{n,m=0}^{\infty}\{\hat{v}_1\cdot\nabla_1\,\mu_1^{(n)}:\nabla_1^n\,\mu_2^{(m)}:\nabla_2^m$$
$$+(\partial_{t\mathrm{P}}\,\mu_1^{(n)}):\nabla_1^n\,\mu_2^{(m)}:\nabla_2^m\}\frac{1}{4\pi|X_1-X_2|}$$
$$+\sum_{n,m=1}^{\infty}[(\nabla_1^{n-1}:\nu_1^{(n)}\wedge\nabla_1)\cdot\{\nabla_2^{m-1}:(\partial_{t\mathrm{P}}\,\nu_2^{(m)})\wedge\nabla_1\}$$
$$-\hat{v}_2\cdot\nabla_1(\nabla_1^{n-1}:\nu_1^{(n)}\wedge\nabla_1)\cdot(\nabla_2^{m-1}:\nu_2^{(m)}\wedge\nabla_1)$$
$$-(v_1-v_2)\cdot\nabla_1(\nabla_1^{n-1}:\nu_{1,\mathrm{spin}}^{(n)}\wedge\nabla_1)\cdot(\nabla_2^{m-1}:\nu_2^{(m)}\wedge\nabla_1)$$
$$-\{\nabla_1^{n-1}:(\partial_{t\mathrm{P}}\,\nu_{1,\mathrm{spin}}^{(n)})\wedge\nabla_1\}\cdot(\nabla_2^{m-1}:\nu_2^{(m)}\wedge\nabla_1)$$
$$-(\nabla_1^{n-1}:\nu_{1,\mathrm{spin}}^{(n)}\wedge\nabla_1)\cdot\{\nabla_2^{m-1}:(\partial_{t\mathrm{P}}\,\nu_2^{(m)})\wedge\nabla_1\}]\frac{1}{4\pi|X_1-X_2|}. \quad (60)$$

The short range power density follows from (IX.85). One finds

$$\Psi^{\mathrm{S}} = \mathrm{Sp}\int \{\psi^{\mathrm{S}}(1,2)+v\cdot f^{\mathrm{S}}(1,2)\}\delta(X_1-R)f_2(1,2;t)\mathrm{d}1\,\mathrm{d}2 \quad (61)$$

with the abbreviations f^{S} (37) and

$$\psi^{\mathrm{S}}(1,2) \equiv \sum_{i,j}\Big\{-(\hat{v}_1+\partial_{t\mathrm{P}}\,r_{1i})\cdot\nabla_{1i}+c^{-2}(\partial_{t\mathrm{P}}\,r_{1i})\cdot(\partial_{t\mathrm{P}}\,r_{2j})(\hat{v}_2+\partial_{t\mathrm{P}}\,r_{2j})\cdot\nabla_{1i}$$
$$-\frac{\hbar^2}{2m_{2j}c^2}(\hat{v}_2+\partial_{t\mathrm{P}}\,r_{2j})\cdot\nabla_{1i}(\partial_{t\mathrm{P}}\,r_{1i})\cdot(\sigma_{2j}\wedge\nabla_{1i})$$
$$+\frac{\hbar}{2m_{2j}c^2}(\hat{v}_1+\partial_{t\mathrm{P}}\,r_{1i})\cdot\nabla_{1i}(\partial_{t\mathrm{P}}\,r_{2j})\cdot(\sigma_{2j}\wedge\nabla_{1i})$$
$$-\frac{\hbar}{2m_{1i}c^2}(\hat{v}_1+\partial_{t\mathrm{P}}\,r_{1i})\cdot\nabla_{1i}\,\partial_{t\mathrm{P}}(r_{1i}-r_{2j})\cdot(\sigma_{1i}\wedge\nabla_{1i})$$
$$-\frac{\hbar^2}{4m_{1i}m_{2j}c^2}(\hat{v}_1+\partial_{t\mathrm{P}}\,r_{1i})\cdot\nabla_{1i}(\sigma_{1i}\wedge\nabla_{1i})\cdot(\sigma_{2j}\wedge\nabla_{1i})\Big\}\frac{e_{1i}e_{2j}}{4\pi|X_{1i}-X_{2j}|}$$
$$-\psi^{\mathrm{C}}(1,2). \quad (62)$$

If the system is sufficiently homogeneous and if no long range correlations are present, one may employ an Irving–Kirkwood procedure and the identity (9) to write both the correlation and short range power density as the sum of a divergence and a time derivative. In this way one finds for the correlation power density

$$\Psi^{C} = -\nabla\cdot(\boldsymbol{v}\varrho u^{C}+\mathbf{P}^{C}\cdot\boldsymbol{v}+\boldsymbol{J}_q^{C})-\frac{\partial\varrho u^{C}}{\partial t}. \qquad (63)$$

Here u^{C} is the correlation contribution to the internal energy density

$$\varrho u^{C} \equiv \mathrm{Sp}\int \varphi^{C}(1,2)\delta\{\tfrac{1}{2}(\boldsymbol{X}_1+\boldsymbol{X}_2)-\boldsymbol{R}\}c_2(1,2;t)\mathrm{d}1\,\mathrm{d}2 \qquad (64)$$

with the abbreviation

$$\varphi^{C}(1,2) \equiv \{\sum_{n,m=0}^{\infty} \boldsymbol{\mu}_1^{(n)}:\nabla_1^n\,\boldsymbol{\mu}_2^{(m)}:\nabla_2^m$$
$$-\sum_{n,m=1}^{\infty}(\nabla_1^{n-1}:\boldsymbol{\nu}_{1,\mathrm{orb}}^{(n)}\wedge\nabla_1)\cdot(\nabla_2^{m-1}:\boldsymbol{\nu}_{2,\mathrm{orb}}^{(m)}\wedge\nabla_1)$$
$$+\sum_{n,m=1}^{\infty}(\nabla_1^{n-1}:\boldsymbol{\nu}_{1,\mathrm{spin}}^{(n)}\wedge\nabla_1)\cdot(\nabla_2^{m-1}:\boldsymbol{\nu}_{2,\mathrm{spin}}^{(m)}\wedge\nabla_1)\}\frac{1}{8\pi|\boldsymbol{X}_1-\boldsymbol{X}_2|}. \qquad (65)$$

The correlation internal energy density (64) consists hence of three contributions: due to electric multipole–electric multipole, orbital magnetic multipole–orbital magnetic multipole and spin magnetic multipole–spin magnetic multipole contributions. No cross-terms between orbital and spin magnetic multipoles occur, in contrast with the situation for the correlation pressure (42) with (35) and the correlation part of the heat flow which is given by:

$$\boldsymbol{J}_q^{C} \equiv \mathrm{Sp}\int\{\tfrac{1}{2}(\hat{\boldsymbol{v}}_1+\hat{\boldsymbol{v}}_2)\varphi^{C}(1,2)+\tfrac{1}{2}(\boldsymbol{X}_1-\boldsymbol{X}_2)\psi^{C}(1,2)\}$$
$$\delta\{\tfrac{1}{2}(\boldsymbol{X}_1+\boldsymbol{X}_2)-\boldsymbol{R}\}c_2(1,2;t)\mathrm{d}1\,\mathrm{d}2. \qquad (66)$$

Likewise we find for the short range power density

$$\Psi^{S} = -\nabla\cdot(\boldsymbol{v}\varrho u^{S}+\mathbf{P}^{S}\cdot\boldsymbol{v}+\boldsymbol{J}_q^{S})-\frac{\partial\varrho u^{S}}{\partial t}, \qquad (67)$$

where the short range contribution to the energy density is

$$\varrho u^{S} \equiv \mathrm{Sp}\int \varphi^{S}(1,2)\delta\{\tfrac{1}{2}(\boldsymbol{X}_1+\boldsymbol{X}_2)-\boldsymbol{R}\}f_2(1,2;t)\mathrm{d}1\,\mathrm{d}2 \qquad (68)$$

with the abbreviation

$$\varphi^{S}(1,2) \equiv \sum_{i,j}\Big\{1+c^{-2}(\partial_{tP}\boldsymbol{r}_{1i})\cdot(\partial_{tP}\boldsymbol{r}_{2j})+\frac{\hbar}{m_{1i}c^2}(\partial_{tP}\boldsymbol{r}_{1i})\cdot(\boldsymbol{\sigma}_{1i}\wedge\nabla_{1i})$$
$$+\frac{\hbar^2}{4m_{1i}m_{2j}c^2}(\boldsymbol{\sigma}_{1i}\wedge\nabla_{1i})\cdot(\boldsymbol{\sigma}_{2j}\wedge\nabla_{1i})\Big\}\frac{e_{1i}e_{2j}}{8\pi|\boldsymbol{X}_{1i}-\boldsymbol{X}_{2j}|}-\varphi^{C}(1,2) \qquad (69)$$

and where the short range part of the heat flow is

$$\boldsymbol{J}_q^{S} \equiv \mathrm{Sp}\int\{\tfrac{1}{2}(\hat{\boldsymbol{v}}_1+\hat{\boldsymbol{v}}_2)\varphi^{S}(1,2)+\tfrac{1}{2}(\boldsymbol{X}_1-\boldsymbol{X}_2)\psi^{S}(1,2)\}\delta\{\tfrac{1}{2}(\boldsymbol{X}_1+\boldsymbol{X}_2)-\boldsymbol{R}\}$$
$$f_2(1,2;t)\mathrm{d}1\,\mathrm{d}2. \qquad (70)$$

Collecting the results, we obtain as the energy balance equation for a system with short range Wigner correlations as for instance a fluid of neutral atoms

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\varrho v^2+\boldsymbol{v}\cdot\boldsymbol{g}+\varrho u) = -\nabla\cdot\{\boldsymbol{v}(\tfrac{1}{2}\varrho v^2+\boldsymbol{v}\cdot\boldsymbol{g}+\varrho u)+\mathbf{P}\cdot\boldsymbol{v}+\boldsymbol{J}_q\}$$
$$+\frac{\partial\boldsymbol{P}}{\partial t}\cdot\boldsymbol{E}-\boldsymbol{M}\cdot\frac{\partial\boldsymbol{B}}{\partial t}+\frac{\partial}{\partial t}\{\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B}+2c^{-1}\boldsymbol{v}\cdot(\boldsymbol{E}\wedge\boldsymbol{M}_{\mathrm{orb}})\}$$
$$+\nabla\cdot[\boldsymbol{v}\{\boldsymbol{P}\cdot\boldsymbol{E}+\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B}+2c^{-1}\boldsymbol{v}\cdot(\boldsymbol{E}\wedge\boldsymbol{M}_{\mathrm{orb}})\}]. \qquad (71)$$

(The Joule heat term $\boldsymbol{J}\cdot\boldsymbol{E}$ of (55) is absent here because the atoms were taken to be neutral.) This energy balance contains the total specific internal energy

$$u = u^{K}+u^{F}+u^{C}+u^{S} \qquad (72)$$

and the total heat flow

$$\boldsymbol{J}_q = \boldsymbol{J}_q^{K}+\boldsymbol{J}_q^{F}+\boldsymbol{J}_q^{C}+\boldsymbol{J}_q^{S}. \qquad (73)$$

As compared to the non-relativistic theory (v. VII.65)) the left-hand side of (71) contains a new term $\boldsymbol{v}\cdot\boldsymbol{g}$ with the macroscopic velocity and the momentum density $\boldsymbol{g}$ (22) due to the intra-atomic fields. It also appears at the right-hand side in the transport term. Furthermore at the right-hand side two extra terms are present with the macroscopic spin magnetization $\boldsymbol{M}_{\mathrm{spin}}$ and moreover two terms with the macroscopic orbital magnetization $\boldsymbol{M}_{\mathrm{orb}}$, which are coupled to the magnetic and electric fields respectively. Other extra semi-relativistic terms are contained in the expressions for the pressure, the specific energy and the heat flow.

With the use of the Maxwell equations we may cast the balance equation (71) into the form of the following energy conservation law

$$\frac{\partial}{\partial t}\{\tfrac{1}{2}\varrho v^2+\boldsymbol{v}\cdot\boldsymbol{g}+\varrho u+\tfrac{1}{2}E^2+\tfrac{1}{2}B^2-\boldsymbol{M}_{\rm spin}\cdot\boldsymbol{B}-2c^{-1}\boldsymbol{v}\cdot(\boldsymbol{E}\wedge\boldsymbol{M}_{\rm orb})\}$$
$$+\nabla\cdot[\boldsymbol{v}(\tfrac{1}{2}\varrho v^2+\boldsymbol{v}\cdot\boldsymbol{g}+\varrho u)+\mathsf{P}\cdot\boldsymbol{v}+\boldsymbol{J}_q+c\boldsymbol{E}\wedge\boldsymbol{H}$$
$$-\boldsymbol{v}\{\boldsymbol{P}\cdot\boldsymbol{E}+\boldsymbol{M}_{\rm spin}\cdot\boldsymbol{B}+2c^{-1}\boldsymbol{v}\cdot(\boldsymbol{E}\wedge\boldsymbol{M}_{\rm orb})\}]=0. \quad (74)$$

The energy laws for plasmas and for systems with long range correlations may be treated along similar lines, as was done in non-relativistic classical theory. In the case of long range correlations one has to introduce mean correlation functions (v. chapter II, section 5*h*).

d. *The angular momentum balance*

The macroscopic inner angular momentum law will follow from its atomic counterpart (IX.91). In the first place we take half the anticommutator of that equation with $\delta(\boldsymbol{X}_k-\boldsymbol{R})$. This procedure is followed since the Weyl-transformed atomic inner angular momentum (more precisely its spin contribution) does not commute with the delta function. Then one takes the sum over the atoms k and averages with a Wigner function. As a result, one obtains after calculations of the type discussed earlier for the momentum and energy laws, for the balance equation of inner angular momentum

$$\frac{\partial \boldsymbol{S}}{\partial t}=-\nabla\cdot(\boldsymbol{v}\boldsymbol{S}+\mathsf{J}_s)-\boldsymbol{P}_{\rm A}-\boldsymbol{v}\wedge\boldsymbol{g}+\boldsymbol{P}\wedge\boldsymbol{E}+\boldsymbol{M}\wedge\boldsymbol{B}+c^{-1}\boldsymbol{v}\wedge(\boldsymbol{P}\wedge\boldsymbol{B}-\boldsymbol{M}_{\rm orb}\wedge\boldsymbol{E}). \quad (75)$$

Here the inner angular momentum density $\boldsymbol{S}$ is defined as

$$\boldsymbol{S}(\boldsymbol{R},t)=\mathrm{Sp}\int\tfrac{1}{2}\{\boldsymbol{s}_1,\delta(\boldsymbol{X}_1-\boldsymbol{R})\}f_1(1;t)\mathrm{d}1 \quad (76)$$

with the atomic inner angular momentum $\boldsymbol{s}_1$, which is the sum of the four quantities defined in (IX.87–90). At the right-hand side appears the divergence of a convection term $\boldsymbol{v}\boldsymbol{S}$ and an inner angular momentum flow J_s, which may be expressed as a statistical average of atomic quantities. Furthermore as source terms one has in the first place the antisymmetric part $\boldsymbol{P}_{\rm A}\equiv\boldsymbol{\epsilon}:\mathsf{P}$ (with $\boldsymbol{\epsilon}$ the Levi-Civita tensor) of the pressure tensor P (44); secondly the vector product of the macroscopic velocity $\boldsymbol{v}$ and the momentum density contribution $\boldsymbol{g}$ (22), and thirdly four terms with the polarizations and fields.

As compared to the non-relativistic equation (VII.70) with (VII.73) two new terms appear here: a term due to the spin momentum density and a semi-relativistic term due to orbital magnetic dipoles in motion. Moreover the quantities $\boldsymbol{S}$, J_s, $\boldsymbol{P}_{\rm A}$, $\boldsymbol{P}$ and $\boldsymbol{M}$ all contain spin contributions.

The form (75) of the inner angular momentum equation allows us to deduce the conservation law of total angular momentum. In fact the balance equation of orbital angular momentum $\boldsymbol{L}$, which follows from (46) by vector multiplication with $\boldsymbol{R}$, is:

$$\frac{\partial \boldsymbol{L}}{\partial t}=-\nabla\cdot(\boldsymbol{v}\boldsymbol{L}+\mathsf{J}_l)+\boldsymbol{P}_{\rm A}+\boldsymbol{v}\wedge\boldsymbol{g}-\boldsymbol{D}\wedge\boldsymbol{E}-\boldsymbol{B}\wedge\boldsymbol{H}-c^{-1}\boldsymbol{v}\wedge(\boldsymbol{P}\wedge\boldsymbol{B}-\boldsymbol{M}_{\rm orb}\wedge\boldsymbol{E}) \quad (77)$$

with the orbital angular momentum defined as

$$\boldsymbol{L}(\boldsymbol{R},t)=\boldsymbol{R}\wedge\{\varrho\boldsymbol{v}+\boldsymbol{g}+c^{-1}\boldsymbol{E}\wedge(\boldsymbol{B}-\boldsymbol{M}_{\rm orb})\} \quad (78)$$

and the conduction part of the orbital angular momentum flow

$$\mathsf{J}_l=-\mathsf{P}\wedge\boldsymbol{R}-\boldsymbol{D}(\boldsymbol{R}\wedge\boldsymbol{E})-\boldsymbol{B}(\boldsymbol{R}\wedge\boldsymbol{H})-c^{-1}\boldsymbol{v}\boldsymbol{R}\wedge(\boldsymbol{D}\wedge\boldsymbol{B})$$
$$+\boldsymbol{\epsilon}\cdot\boldsymbol{R}(\tfrac{1}{2}E^2+\tfrac{1}{2}B^2-\boldsymbol{M}\cdot\boldsymbol{B}). \quad (79)$$

The total angular momentum law follows by adding (75) and (77):

$$\frac{\partial(\boldsymbol{L}+\boldsymbol{S})}{\partial t}=-\nabla\cdot\{\boldsymbol{v}(\boldsymbol{L}+\boldsymbol{S})+\mathsf{J}_l+\mathsf{J}_s\}, \quad (80)$$

which has indeed the form of a conservation law.

Laws for plasmas and systems with long range correlations may be derived in a similar way.

5 *The laws of thermodynamics*

a. *The first law*

The first law of thermodynamics follows if one subtracts the momentum equation (43) multiplied by the macroscopic velocity $\boldsymbol{v}$ from the energy law (71). If one employs the notation $\mathrm{d}/\mathrm{d}t$ for the material time derivative $\partial/\partial t+\boldsymbol{v}\cdot\nabla$ and the mass conservation law (18), one gets thus

$$\varrho\frac{\mathrm{d}u}{\mathrm{d}t}=-\nabla\cdot\boldsymbol{J}_q-\tilde{\mathsf{P}}:\nabla\boldsymbol{v}-\boldsymbol{g}\cdot\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}+\varrho\frac{\mathrm{d}(v\boldsymbol{P}')}{\mathrm{d}t}\cdot\boldsymbol{E}'-\boldsymbol{M}'\cdot\frac{\mathrm{d}\boldsymbol{B}'}{\mathrm{d}t}$$
$$+\varrho\frac{\mathrm{d}}{\mathrm{d}t}(v\boldsymbol{M}'_{\rm spin}\cdot\boldsymbol{B}')-c^{-1}\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}\cdot(\boldsymbol{E}'\wedge\boldsymbol{M}'_{\rm spin}), \quad (81)$$

where v is the specific volume and where the tilde indicates the transposed of a tensor. The electromagnetic quantities are all counted in the local rest frame:

$$\begin{aligned} \boldsymbol{E}' &= \boldsymbol{E}+c^{-1}\boldsymbol{v}\wedge\boldsymbol{B}, \qquad & \boldsymbol{B}' &= \boldsymbol{B}-c^{-1}\boldsymbol{v}\wedge\boldsymbol{E}, \\ \boldsymbol{P}' &= \boldsymbol{P}-c^{-1}\boldsymbol{v}\wedge\boldsymbol{M}, \qquad & \boldsymbol{M}' &= \boldsymbol{M}+c^{-1}\boldsymbol{v}\wedge\boldsymbol{P}. \end{aligned} \tag{82}$$

($\boldsymbol{M}_{\text{spin}}$ could be replaced by $\boldsymbol{M}'_{\text{spin}}$ since the difference is of order c^{-3}.)

The law (81) is valid for fluid systems of neutral atoms. Amorphous or polycrystalline solids, plasmas and systems with long range correlations may be treated in a similar way.

b. *The second law*

To derive the second law for a fluid system of neutral atoms in which only short range Wigner correlations are present we shall apply the canonical ensemble method to a nearly uniform sample of ellipsoidal shape which is at rest in a large polarized system. Then the external fields due to the surroundings of the sample are uniform and given by (II.220) with (II.219). The Hamilton operator H_{op} which is to be used, is derived in appendix I and given by (A1) with (A9), with atomic charges $e_k = 0$. We denote its Weyl transform as $H(1, \ldots, N)$.

The partial derivatives of the free energy F^* with respect to the external fields may be expressed as averages involving the partial derivatives of the Weyl transform of the Hamiltonian:

$$\begin{aligned} \frac{\partial F^*}{\partial \boldsymbol{E}_e} &= \mathrm{Sp}\int \frac{\partial H}{\partial \boldsymbol{E}_e}\rho(1,\ldots,N)\mathrm{d}1\ldots\mathrm{d}N, \\ \frac{\partial F^*}{\partial \boldsymbol{B}_e} &= \mathrm{Sp}\int \frac{\partial H}{\partial \boldsymbol{B}_e}\rho(1,\ldots,N)\mathrm{d}1\ldots\mathrm{d}N, \end{aligned} \tag{83}$$

where $\rho(1, \ldots, N)$ is the Wigner function of the canonical ensemble. From the explicit form of the Weyl transform of the Hamilton operator (A1) with (A9) it follows that

$$\begin{aligned} \frac{\partial F^*}{\partial \boldsymbol{E}_e} &= -\mathrm{Sp}\int \left(\bar{\boldsymbol{\mu}}^{(1)}_{1,\text{orb}} - \tfrac{1}{2}c^{-1}\boldsymbol{v}^{(1)}_{1,\text{spin}}\wedge\frac{\boldsymbol{P}_1}{m_1} + \tfrac{1}{2}\boldsymbol{\mu}^{(1)}_{1,\text{spin}}\right) f_1(1)\mathrm{d}1, \\ \frac{\partial F^*}{\partial \boldsymbol{B}_e} &= -\mathrm{Sp}\int \left\{\boldsymbol{v}^{(1)}_1 + \tfrac{1}{2}c^{-1}\boldsymbol{\mu}^{(1)}_{1,\text{orb}}\wedge\frac{\boldsymbol{P}_1}{m_1} - \tfrac{1}{2}c^{-1}(\partial_{t\mathrm{P}}\boldsymbol{\mu}^{(1)}_{1,\text{orb}})\wedge\boldsymbol{R}_1\right\} f_1(1)\mathrm{d}1. \end{aligned} \tag{84}$$

The bar in the first of these formulae denotes an orbital electric dipole moment that is defined in a non-relativistic fashion, i.e. in terms of the coordinates $\boldsymbol{R}_{ki}$ of the constituent particles (v. appendix I). This non-relativistic dipole moment may be expressed in terms of the semi-relativistic ones by means of the identity (A10). Then the first relation of (84) gets the form

$$\frac{\partial F^*}{\partial \boldsymbol{E}_e} = -\mathrm{Sp}\int \left(\boldsymbol{\mu}^{(1)}_1 - c^{-1}\boldsymbol{v}^{(1)}_1\wedge\frac{\boldsymbol{P}_1}{m_1}\right) f_1(1)\mathrm{d}1 = -V\boldsymbol{P}, \tag{85}$$

where the uniformity of the system has been taken into account, so that the volume V times the polarization $\boldsymbol{P}$ appears. The second relation of (84) may be transformed if one uses the stationarity of the canonical ensemble in the same way as has been done in the non-relativistic treatment (v. (VII.89)). Then it gets the form:

$$\frac{\partial F^*}{\partial \boldsymbol{B}_e} = -\mathrm{Sp}\int \left(\boldsymbol{v}^{(1)}_1 + c^{-1}\boldsymbol{\mu}^{(1)}_1\wedge\frac{\boldsymbol{P}_1}{m_1}\right) f_1(1)\mathrm{d}1 = -V\boldsymbol{M} \tag{86}$$

with $\boldsymbol{M}$ the macroscopic magnetization. (A term with spin electric dipole moments $\boldsymbol{\mu}^{(1)}_{1,\text{spin}}$ in motion is added for reasons of elegance, although it leads to a term of order c^{-3} only.)

Since the change of free energy depends on changes in temperature, external fields and position of the boundary (specified by the deformation tensor $\delta\boldsymbol{\epsilon}$, see for instance (VII.92)), one may write

$$\delta F^* = -S\delta T - V\boldsymbol{P}\cdot\delta\boldsymbol{E}_e - V\boldsymbol{M}\cdot\delta\boldsymbol{B}_e + \mathbf{A} : \delta\boldsymbol{\epsilon}, \tag{87}$$

where $S = -\partial F^*/\partial T$ is the entropy. The second law will follow by establishing the statistical expressions for the free energy F^* and the tensor $\mathbf{A}$.

The free energy may be obtained from the average of the Hamilton operator of the system. From the expression (A6) with (A11) for the Hamiltonian one finds in semi-relativistic approximation, by comparison with the expressions (52), (57), (64) and (68) for the various parts of the internal energy, for the average Hamiltonian $\langle H\rangle \equiv U^*$:

$$U^* = U + V\{\tfrac{1}{2}(\boldsymbol{PP}-\boldsymbol{MM}) : \mathbf{L} - \boldsymbol{P}\cdot\boldsymbol{E}_e + \tfrac{1}{2}M^2 - \boldsymbol{M}_{\text{spin}}\cdot(\boldsymbol{B}_e+\boldsymbol{M}) + \boldsymbol{M}_{\text{spin}}\boldsymbol{M} : \mathbf{L}\}. \tag{88}$$

Here U is the internal energy $V\varrho u$ with ϱ the mass density and $\mathbf{L}$ the depolarizing tensor defined in (II.219).

Finally we consider the tensor $\mathbf{A}$, which is given in the appendix II (A23) as the statistical expression

$$\mathbf{A} = -\mathrm{Sp}\int \sum_k \partial_{t\mathrm{P}}(\boldsymbol{X}_k\boldsymbol{P}_k)\rho(1,\ldots,N)\mathrm{d}1\ldots\mathrm{d}N, \tag{89}$$

where ∂_{tP} denotes the Poisson bracket with the Weyl transform H of the Hamiltonian (A1) with (A9). With $\boldsymbol{v}_k = \partial_{tP}\boldsymbol{X}_k$ we may write (89) as

$$\mathbf{A} = -\mathrm{Sp}\int \sum_k (\boldsymbol{v}_k\boldsymbol{P}_k + \boldsymbol{X}_k\partial_{tP}\boldsymbol{P}_k)\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N. \tag{90}$$

The velocity $\boldsymbol{v}_k$ may be calculated with the help of the explicit expressions for $\boldsymbol{X}_k$ and H (v. (IX.40)). One finds then, in semi-relativistic approximation,

$$\boldsymbol{P}_k = m_k\boldsymbol{v}_k + \boldsymbol{g}_k - \tfrac{1}{2}c^{-1}\boldsymbol{\mu}_k^{(1)}\wedge\boldsymbol{B}_e + c^{-1}\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge\boldsymbol{E}_e$$
$$+c^{-2}\sum_{l(\neq k)}\sum_{i,j}\{(\partial_{tP}\boldsymbol{r}_{lj})\cdot\mathsf{T}(\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}) + 2\boldsymbol{r}_{ki}(\partial_{tP}\boldsymbol{r}_{ki})\cdot\nabla_{ki}\}\frac{e_{ki}e_{lj}}{8\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}|}$$
$$-c^{-2}\sum_{l(\neq k)}\sum_{i,j}{}'\frac{\hbar}{2m_{lj}}\boldsymbol{\sigma}_{lj}\wedge\nabla_{ki}\frac{e_{ki}e_{lj}}{4\pi|\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}|}, \tag{91}$$

where $\boldsymbol{g}_k$ has been given in (IX.69). The quantity $\partial_{tP}\boldsymbol{P}_k$ in the second term of (90) is equal to $-\partial H/\partial\boldsymbol{R}_k$ and may hence be evaluated explicitly. In this way one finds for the tensor $\mathbf{A}$ in semi-relativistic approximation, by comparing with the expressions (25), (33), (40) and (42) for the pressure tensor,

$$\mathbf{A} = -V\{\mathbf{P} + \tfrac{1}{2}\mathbf{K} : (\boldsymbol{PP}+\boldsymbol{MM}) - \tfrac{1}{2}M^2\mathbf{U}\}, \tag{92}$$

where $\mathbf{K}$ is the tensor defined in (II.236). In the course of the derivation of (92) one needs to apply the stationarity of the canonical ensemble.

Substituting the expression (88) for U^*, which is equal to F^*+TS, and the expression (92) for the tensor $\mathbf{A}$ into the relation (87) one finds, upon dividing through the conserved total mass ϱV of the system:

$$\delta[u + v\{\tfrac{1}{2}(\boldsymbol{PP}-\boldsymbol{MM}) : \mathbf{L} + \tfrac{1}{2}M^2 - \boldsymbol{M}_{\mathrm{spin}}\cdot(\boldsymbol{B}_e+\boldsymbol{M}) + \boldsymbol{M}_{\mathrm{spin}}\boldsymbol{M} : \mathbf{L}\}]$$
$$= T\delta s + \boldsymbol{E}_e\cdot\delta(v\boldsymbol{P}) - v\boldsymbol{M}\cdot\delta\boldsymbol{B}_e$$
$$-v\{\mathbf{P} + \tfrac{1}{2}\mathbf{K} : (\boldsymbol{PP}+\boldsymbol{MM}) - \tfrac{1}{2}M^2\mathbf{U}\} : \delta\boldsymbol{\epsilon}, \tag{93}$$

where v and s are the specific volume and entropy.

If one makes use of the relation (II.220) one may eliminate the external fields in favour of the Maxwell fields. With the help of (II.246) one finds then for the change of the entropy the relation

$$T\delta s = \delta u + v\mathbf{P} : \delta\boldsymbol{\epsilon} - \boldsymbol{E}\cdot\delta(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\delta\boldsymbol{B} - \delta(v\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B}). \tag{94}$$

One notices that the specific internal energy appears in combination with a magnetic energy term $-v\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B}$, just as in the first law (81).

For an isotropic fluid one may argue that under certain conditions (v. chapter II, section 7*b*) the pressure tensor $\mathbf{P}$ reduces in equilibrium to a

multiple of the unit tensor $p\mathbf{U}$ with p the (scalar) pressure. Then we may finally write (94) for such systems in the form of a Gibbs relation

$$T\mathrm{d}s = \mathrm{d}(u - v\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B}) + p\,\mathrm{d}v - \boldsymbol{E}\cdot\mathrm{d}(v\boldsymbol{P}) + v\boldsymbol{M}\cdot\mathrm{d}\boldsymbol{B}, \tag{95}$$

where we have written differentials instead of variations, since only state variables are involved now.

The derivation of the second law for amorphous or polycrystalline solids, neutral plasmas and systems with long range correlations such as crystalline solids may be performed in a way similar to that given above for fluid systems with short range correlations. In the following we shall indicate which new features arise for the case with long range correlations. Just as in the non-relativistic treatment of chapter II, we consider a sample at rest without macroscopic charge and current densities although we allow for the atoms carrying electric charges. Under those circumstances the system is characterized by a free energy with partial derivatives with respect to the external fields

$$\frac{\partial F^*}{\partial\boldsymbol{E}_e} = -\int\boldsymbol{P}(\boldsymbol{R})\mathrm{d}\boldsymbol{R} \equiv -V\overline{\boldsymbol{P}},$$
$$\frac{\partial F^*}{\partial\boldsymbol{B}_e} = -\int\boldsymbol{M}(\boldsymbol{R})\mathrm{d}\boldsymbol{R} \equiv -V\overline{\boldsymbol{M}}. \tag{96}$$

The right-hand sides are written as integrals (or in terms of volume averages (II.280) indicated by bars over the symbols) since the polarizations of the system are not necessarily uniform in the present case.

For the average Hamiltonian $U^* \equiv \langle H\rangle$ we find, using again the fact that the charge density vanishes,

$$U^* = U - \int\{\boldsymbol{P}(\boldsymbol{R}_1)\boldsymbol{P}(\boldsymbol{R}_2) - \boldsymbol{M}(\boldsymbol{R}_1)\boldsymbol{M}(\boldsymbol{R}_2) + 2\boldsymbol{M}(\boldsymbol{R}_1)\boldsymbol{M}_{\mathrm{spin}}(\boldsymbol{R}_2)\}$$
$$: \nabla_1\nabla_1\frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2 - V\overline{\boldsymbol{P}}\cdot\boldsymbol{E}_e + \tfrac{1}{2}V\overline{M^2}$$
$$-V\overline{\boldsymbol{M}}_{\mathrm{spin}}\cdot\boldsymbol{B}_e - V\overline{\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{M}}. \tag{97}$$

Here U is the total internal energy $\int\varrho u\,\mathrm{d}V$, with ϱu the internal energy density, which occurs in the local energy balance equation for a system with long range correlations. (This balance equation has the same form as that for systems with short range correlations, v. (71), with the only difference that the correlation contributions to the heat flow and the pressure tensor contain mean correlation functions. A similar situation arose already in the classical non-relativistic theory.)

For the change $\delta_\varepsilon F^*$ of the free energy under deformations one finds by a reasoning analogous to that which led to formula (II.289) of the non-relativistic treatment of chapter II the result

$$\delta_\varepsilon F^* = -\int \mathbf{P}(\boldsymbol{R}) : \delta\mathbf{e}(\boldsymbol{R})\mathrm{d}\boldsymbol{R}$$
$$-\int \{\boldsymbol{R}_1\cdot\delta\bar{\boldsymbol{\epsilon}}(\boldsymbol{R}_1)-\boldsymbol{R}_2\cdot\delta\bar{\boldsymbol{\epsilon}}(\boldsymbol{R}_2)\}\cdot[\boldsymbol{P}(\boldsymbol{R}_1)\boldsymbol{P}(\boldsymbol{R}_2) : \nabla_1\nabla_1$$
$$-\{\boldsymbol{M}(\boldsymbol{R}_1)\wedge\nabla_1\}\cdot\{\boldsymbol{M}(\boldsymbol{R}_2)\wedge\nabla_1\}]\nabla_1 \frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2 \quad (98)$$

with $\delta\mathbf{e}$ the deformation gradient tensor (II.A51). As compared to the classical non-relativistic result (II.289) an additional term quadratic in the magnetization appears here. It may be written in the alternative form

$$-\int \{\boldsymbol{R}_1\cdot\delta\bar{\boldsymbol{\epsilon}}(\boldsymbol{R}_1)-\boldsymbol{R}_2\cdot\delta\bar{\boldsymbol{\epsilon}}(\boldsymbol{R}_2)\}\boldsymbol{M}(\boldsymbol{R}_1)\boldsymbol{M}(\boldsymbol{R}_2) \,\vdots\, \nabla_1\nabla_1\nabla_1 \frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2$$
$$+\tfrac{1}{2}\int \{\mathrm{Tr}\ \delta\mathbf{e}(\boldsymbol{R}_1)\}\{\boldsymbol{M}(\boldsymbol{R}_1)\}^2\mathrm{d}\boldsymbol{R}_1. \quad (99)$$

The entropy law that follows from (96–99) reads:

$$T\delta S = \delta U + \int \mathbf{P}(\boldsymbol{R}) : \delta\mathbf{e}(\boldsymbol{R})\mathrm{d}\boldsymbol{R} - \boldsymbol{E}_e\cdot\delta(V\overline{\boldsymbol{P}})$$
$$+V\overline{\boldsymbol{M}}\cdot\delta\boldsymbol{B}_e - \delta\Bigg[\int \{\boldsymbol{P}(\boldsymbol{R}_1)\boldsymbol{P}(\boldsymbol{R}_2)-\boldsymbol{M}(\boldsymbol{R}_1)\boldsymbol{M}(\boldsymbol{R}_2)$$
$$+2\boldsymbol{M}(\boldsymbol{R}_1)\boldsymbol{M}_{\mathrm{spin}}(\boldsymbol{R}_2)\} : \nabla_1\nabla_1 \frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2$$
$$-\tfrac{1}{2}V\overline{\boldsymbol{M}^2}+V\overline{\boldsymbol{M}_{\mathrm{spin}}\cdot(\boldsymbol{B}_e+\boldsymbol{M})}\Bigg]$$
$$+\int \{\boldsymbol{R}_1\cdot\delta\bar{\boldsymbol{\epsilon}}(\boldsymbol{R}_1)-\boldsymbol{R}_2\cdot\delta\bar{\boldsymbol{\epsilon}}(\boldsymbol{R}_2)\}\{\boldsymbol{P}(\boldsymbol{R}_1)\boldsymbol{P}(\boldsymbol{R}_2)+\boldsymbol{M}(\boldsymbol{R}_1)\boldsymbol{M}(\boldsymbol{R}_2)\} \,\vdots\, \nabla_1\nabla_1\nabla_1$$
$$\frac{1}{8\pi|\boldsymbol{R}_1-\boldsymbol{R}_2|}\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2 - \tfrac{1}{2}V\overline{(\mathrm{Tr}\ \delta\mathbf{e})\boldsymbol{M}^2}. \quad (100)$$

Along similar lines as followed in chapter II to obtain (II.302) from (II.296) one may introduce the Maxwell fields instead of the external fields, using (II.220). Then one gets for the entropy law

$$T\delta S = \delta U + V\overline{\mathbf{P} : \delta\mathbf{e}} - V\overline{\boldsymbol{E}\cdot\delta\boldsymbol{P}} + V\overline{\boldsymbol{M}\cdot\delta\boldsymbol{B}} - V\overline{\delta(\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B})}$$
$$-V\overline{(\mathrm{Tr}\ \delta\mathbf{e})(\boldsymbol{P}\cdot\boldsymbol{E}+\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B})}, \quad (101)$$

again with a bar notation for volume averages. By performing a partial integration in the integral represented by the second term at the right-hand side this equation may be written in the form (cf. (II.304)):

$$T\delta S = \delta U + \int^S \boldsymbol{n}\cdot\{\mathbf{P}\cdot\delta\boldsymbol{\epsilon}\cdot\boldsymbol{R} - \delta\boldsymbol{\epsilon}\cdot\boldsymbol{R}(\boldsymbol{P}\cdot\boldsymbol{E}+\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B})\}\mathrm{d}S$$
$$-\int \{\boldsymbol{E}\cdot\delta_0\boldsymbol{P} - \boldsymbol{M}\cdot\delta_0\boldsymbol{B} + \delta_0(\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B})\}\mathrm{d}\boldsymbol{R}, \quad (102)$$

where we used the equation of motion (43) which reads in the present case

$$\nabla\cdot\mathbf{P} = (\nabla\boldsymbol{E})\cdot\boldsymbol{P} + (\nabla\boldsymbol{B})\cdot\boldsymbol{M}. \quad (103)$$

If the system is not rotated and if it is only slightly deformed, one may replace $\delta\boldsymbol{\epsilon}$ by the change $\delta\boldsymbol{\eta}$ of state variable $\boldsymbol{\eta}$ according to (II.311). Furthermore, if the system is chosen to have ellipsoidal shape, the uniform external fields cause polarizations and Maxwell fields that are nearly uniform. Then one finds from the entropy law (102) the Gibbs relation

$$T\mathrm{d}S = \mathrm{d}(U - V\boldsymbol{M}_{\mathrm{spin}}\cdot\boldsymbol{B}) + \int^S \boldsymbol{n}\cdot\mathbf{P}(\boldsymbol{R})\cdot\mathrm{d}\boldsymbol{\eta}(\boldsymbol{R})\cdot\boldsymbol{R}\,\mathrm{d}S$$
$$-\boldsymbol{E}\cdot\mathrm{d}(V\boldsymbol{P}) + V\boldsymbol{M}\cdot\mathrm{d}\boldsymbol{B}, \quad (104)$$

where we have written differentials since now the (uniform) Maxwell fields and the polarizations may be considered as state variables. Comparison with (II.321) shows that the only difference is that a magnetic spin term is present in the Gibbs relation (104) (v. also (95) for fluids).

6 *Applications*

On the basis of the energy–momentum equations and the laws of thermodynamics, derived in the preceding in the semi-relativistic approximation for systems with spin, one may derive now expressions for the pressure in the presence and in the absence of electromagnetic fields, i.e. the Kelvin and Helmholtz pressures (cf. chapter II, section 8). A special application of the general theory, namely the calculation of the magnetostriction in a simple model for a crystalline solid, will be treated in the following. In chapter II it was shown that the total electrostriction could be split into a so-called 'form effect' due to the outward and Liénard pressures and the proper electrostrictive phenomenon. A similar splitting may be made in the case of magnetostriction. Just as in (II.239–241) one may find the Liénard pressure, which gives the difference between the pressure just inside and just outside the boundary of a magnetized system. One finds

$$\boldsymbol{n}\cdot(\mathbf{P}-\mathbf{P}_{\text{out}}) = -\tfrac{1}{2}n(\boldsymbol{M}\cdot\boldsymbol{n})^2+\tfrac{1}{2}\boldsymbol{n}M^2. \tag{105}$$

From this expression one obtains for the normal component of the pressure tensor $\mathbf{P}_0$ in the absence of fields, but with the same deformation at the surface and at the same temperature

$$\boldsymbol{n}\cdot\mathbf{P}_0(\boldsymbol{R}) = \boldsymbol{n}\cdot\mathbf{P}_{\text{out}}(\boldsymbol{R})-\tfrac{1}{2}\boldsymbol{n}(\boldsymbol{M}\cdot\boldsymbol{n})^2-\tfrac{1}{2}\boldsymbol{BB}:\boldsymbol{\chi}_1(\boldsymbol{R},T)-\tfrac{1}{2}\boldsymbol{n}\boldsymbol{M}\cdot\boldsymbol{H} \tag{106}$$

(cf. (II.390)), for a uniformly magnetized ellipsoid of which the magnetization fulfils a linear relation (II.384) with (II.385). The magnetization of a paramagnetic substance is described by such a law, at least in a certain approximation. The first two terms of (106) are conventionally called the pressure corresponding to the form effect, while the (uniform) proper magnetostriction is determined by the pressure tensor

$$-\tfrac{1}{2}\boldsymbol{BB}:\hat{\boldsymbol{\chi}}_1(T)-\tfrac{1}{2}\boldsymbol{M}\cdot\boldsymbol{H}\mathbf{U}, \tag{107}$$

where (II.391) has been used. The central quantity that is to be calculated is $\hat{\boldsymbol{\chi}}_1(T)$, which fulfils, according to its definition, the relation

$$\chi^{ij}(\boldsymbol{\eta},T) = \chi_0^{ij}(T)+\hat{\chi}_1^{ijlk}(T)\eta_{kl} \tag{108}$$

for uniform and small deformations, determined by η_{kl}.

Let us study the proper magnetostriction for the following model[1] of a magnetizable crystalline solid: spin magnetic dipoles $\boldsymbol{v}_k$ are situated on the lattice points k of a simple cubic lattice. The Hamilton operator for such a system in a uniform time-independent, external field $\boldsymbol{B}_e$ follows from (A1) with (A9). Due to the combined action of the Pauli exclusion principle and the Coulomb interactions an effective 'exchange coupling' between spin magnetic moments of neighbouring atoms arises, so that the total effective spin Hamilton operator has the form

$$H_{\text{op}}(1,\ldots,N) \rightleftarrows -\sum_{k,l(k\neq l)}(\boldsymbol{v}_k\wedge\nabla_k)\cdot(\boldsymbol{v}_l\wedge\nabla_l)\frac{1}{8\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|} +\tfrac{1}{2}\sum_{k,l(k\neq l)}v_{kl}\,\boldsymbol{v}_k\cdot\boldsymbol{v}_l-\sum_k\boldsymbol{v}_k\cdot\boldsymbol{B}_e \tag{109}$$

with v_{kl} the exchange interaction which is different from zero for neighbouring atoms k and l only.

[1] L. Néel, J. Phys. Radium **15**(1954)225.

The magnetization of such a spin system will be calculated now in the high temperature limit[1], i.e. by writing first a series expansion of the energy in powers of $\beta = (kT)^{-1}$:

$$F = -\beta^{-1}\ln\{\mathrm{Tr}\,e^{-\beta H_{\text{op}}}\} = -\beta^{-1}\ln\{\mathrm{Tr}\,(I-\beta H_{\text{op}}+\tfrac{1}{2}\beta^2H_{\text{op}}^2+\ldots)\}. \tag{110}$$

Here Tr I is the trace of the unit operator in Hilbert space; it is equal to the sum $(2s+1)N$ of all states (s is the spin of the atoms). From the form (109) of the Hamilton operator it follows that its trace vanishes, so that one may write for the free energy (110) up to order β^2:

$$F = -\beta^{-1}\ln(\mathrm{Tr}\,I)-\tfrac{1}{2}\beta\frac{\mathrm{Tr}\,(H_{\text{op}}^2)}{\mathrm{Tr}\,I}+\tfrac{1}{6}\beta^2\frac{\mathrm{Tr}\,(H_{\text{op}}^3)}{\mathrm{Tr}\,I}. \tag{111}$$

The field dependent part of the second term is equal to

$$-\tfrac{1}{6}\beta Nv^2\boldsymbol{B}_e^2 \tag{112}$$

with $v \equiv (e\hbar/mc)\{s(s+1)\}^{\frac{1}{2}}$ the magnitude of the atomic magnetic dipole moment (with $g = 2$, since the orbital magnetic moments do not play a role here). Furthermore the field dependent part of the third term of (111) is

$$-\tfrac{1}{18}\beta^2v^4\sum_{k,l(k\neq l)}\left\{(\boldsymbol{B}_e\wedge\nabla_k)\cdot(\boldsymbol{B}_e\wedge\nabla_l)\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}-v_{kl}\boldsymbol{B}_e^2\right\}. \tag{113}$$

For an ellipsoidal system the sum over l for fixed k may be split into a part that is a sum over the lattice points inside a sphere around k (containing many atoms, but small compared to the system as a whole) and a remaining term which may be approximated by an integral. Then one finds for (113)

$$\tfrac{1}{18}\beta^2\frac{N^2}{V}v^4(\mathbf{L}-\tfrac{1}{3}\mathbf{U}+\mathbf{S}_1):\boldsymbol{B}_e\boldsymbol{B}_e, \tag{114}$$

where $\mathbf{L}$ is the depolarizing tensor (II.219) and where we employed the (approximate) uniformity of the ellipsoidal system. Furthermore we introduced the lattice sum $\mathbf{S}_1$ defined as:

$$\mathbf{S}_1 \equiv -\frac{V}{N}\sum_{l(\neq k)}^{\text{sph}}\left(\nabla_k\nabla_k\frac{1}{4\pi|\boldsymbol{R}_k-\boldsymbol{R}_l|}-v_{kl}\mathbf{U}\right). \tag{115}$$

(For undeformed cubic lattices the first term in this lattice sum does not contribute. However since we shall consider deformations in the following, it may not be suppressed here.)

[1] J. H. Van Vleck, J. Chem. Phys. **5**(1937)320.

The magnetization up to order β^2 follows from the field dependent part of the free energy, given by the sum of (112) and (114):

$$\boldsymbol{M} = -\frac{1}{V}\frac{\partial F}{\partial \boldsymbol{B}_e} = \tfrac{1}{3}\beta \frac{N}{V} \nu^2 \boldsymbol{B}_e - \tfrac{1}{9}\beta^2 \left(\frac{N}{V}\right)^2 \nu^4 (\mathbf{L} - \tfrac{1}{3}\mathbf{U} + \mathbf{S}_1) \cdot \boldsymbol{B}_e . \qquad (116)$$

Introducing the Maxwell field $\boldsymbol{B}$ by means of (II.220) one finds up to order β^2:

$$\boldsymbol{M} = \boldsymbol{\chi} \cdot \boldsymbol{B} \qquad (117)$$

with the susceptibility tensor

$$\boldsymbol{\chi}(T) = \tfrac{1}{3}\beta \frac{N}{V} \nu^2 \mathbf{U} - \tfrac{2}{27}\beta^2 \left(\frac{N}{V}\right)^2 \nu^4 \mathbf{U} - \tfrac{1}{9}\beta^2 \left(\frac{N}{V}\right)^2 \nu^4 \mathbf{S}_1 . \qquad (118)$$

To find the magnetostriction we have to calculate the change of this susceptibility tensor under uniform deformations $\delta \boldsymbol{R} = \delta \boldsymbol{\eta} \cdot \boldsymbol{R}$ with a symmetric tensor $\delta \boldsymbol{\eta}$. The change of volume is then given by $\delta V = V \operatorname{Tr} \delta \boldsymbol{\eta}$. Furthermore the change of the lattice sum $\mathbf{S}_1$ (115) under such deformations may be written as

$$\delta\left(\frac{N}{V}\mathbf{S}_1\right) = -\frac{N}{V}(\delta \mathbf{L})^{\mathrm{sph}} - \sum_{l(\neq k)}^{\mathrm{sph}} \left\{ (\boldsymbol{R}_k - \boldsymbol{R}_l) \cdot \delta \boldsymbol{\eta} \cdot \nabla_k \nabla_k \nabla_k \frac{1}{4\pi |\boldsymbol{R}_k - \boldsymbol{R}_l|} - \delta v_{kl} \mathbf{U} \right\} . \qquad (119)$$

The first term follows from (II.A25). Performing the differentiations in the second term and using the relations

$$\overline{\alpha_i \alpha_j} = \tfrac{1}{3}\delta_{ij} ,$$
$$\overline{\alpha_i \alpha_j \alpha_k \alpha_l} = -\tfrac{1}{2}\delta_{ij}\delta_{ik}\delta_{il} + \tfrac{5}{2}\delta_{ij}\delta_{ik}\delta_{il}\overline{\alpha_1^4} + (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})(\tfrac{1}{6} - \tfrac{1}{2}\overline{\alpha_1^4}) \qquad (120)$$

for averages over angles of the direction cosines $\alpha_i \equiv R_i/R$ $(i = 1, 2, 3)$ (with respect to the cubic axes) of the radius vectors $\boldsymbol{R}$ $(\equiv \boldsymbol{R}_l - \boldsymbol{R}_k)$ from a fixed lattice point k to the other points l, one finds for the ij-component of (119):

$$\delta\left(\frac{N}{V} S_1^{ij}\right) = \frac{N}{V}\{\tfrac{2}{5}\delta\eta^{ij} - \tfrac{2}{15}\delta^{ij} \operatorname{Tr} \delta\boldsymbol{\eta} + S_2(\tfrac{3}{2}\delta^{ij} \operatorname{Tr} \delta\boldsymbol{\eta} + 3\delta\eta^{ij} - \tfrac{15}{2}\delta^{ij}\delta\eta^{ii}) + \mathbf{S}_3 : \delta\boldsymbol{\eta}\delta^{ij}\} \qquad (121)$$

with the lattice sums

$$S_2 \equiv \frac{V}{N}\sum_{\boldsymbol{R}}^{\mathrm{sph}} (1 - 5\alpha_1^4) \frac{1}{4\pi R^3} ,$$
$$\mathbf{S}_3 \equiv \frac{V}{N}\sum_{\boldsymbol{R}}^{\mathrm{sph}} \frac{\partial v(\boldsymbol{R})}{\partial \boldsymbol{\eta}} , \qquad (122)$$

where v^{kl} has been written now as a function $v(\boldsymbol{R})$. Substituting the result (121) into the formula that follows from (118) by variation one finds that $\delta\boldsymbol{\chi}$ is given by an expression like the second term of (108) with a fourth rank tensor $\hat{\boldsymbol{\chi}}$:

$$\hat{\chi}^{ijkl}(T) = -\tfrac{1}{3}\beta \frac{N}{V} \nu^2 \delta^{ij}\delta^{kl} + \beta^2 \left(\frac{N}{V}\right)^2 \nu^4 \{\tfrac{22}{135}\delta^{ij}\delta^{kl} - \tfrac{2}{45}\delta^{ik}\delta^{jl} + \tfrac{1}{9}S_1^{ij}\delta^{kl} - \tfrac{1}{6}S_2(\delta^{ij}\delta^{kl} + 2\delta^{ik}\delta^{jl} - 5\delta^{ij}\delta^{ik}\delta^{il}) - \tfrac{1}{9}S_3^{kl}\delta^{ij}\}. \qquad (123)$$

For the pressure (107) that causes the proper magnetostriction one obtains now with (117–118), again up to order β^2,

$$\tfrac{1}{5}M^i M^j + \tfrac{1}{10}\boldsymbol{M}^2\delta^{ij} + \tfrac{3}{4}S_2(\boldsymbol{M}^2\delta^{ij} + 2M^i M^j - 5M^{i2}\delta^{ij}) + \tfrac{1}{2}S_3^{ij}\boldsymbol{M}^2. \qquad (124)$$

The first three terms together form the dipole–dipole contribution, which is often called the classical magnetostriction[1], while the last term represents the exchange interaction contribution. The lattice sum S_2, which is a purely geometrical quantity, may easily be computed. The lattice sum $\mathbf{S}_3$ contains the partial derivatives of the exchange quantities v_{kl} with respect to the components of the deformation tensor; only rough estimates can be given for its magnitude.

From the expression (124) for the pressure that causes the proper magnetostriction one may calculate the corresponding strains along the standard lines of elasticity theory (for the field free case, since (124) is a contribution to the Helmholtz pressure tensor). Then one obtains expressions for the conventionally defined[2] magnetostriction constants. The results, generalized for the proper lattices, are not in agreement with experiments. The reason for this is that effects due to spin–orbit coupling have not been taken into account[3]. The preceding treatment was meant only to give an introduction to the theory of magnetostriction.

[1] N. Akulov, Z. Physik **52**(1928)389; R. Becker, Z. Physik **62**(1930)253; F. C. Powell, Proc. Cambr. Phil. Soc. **27**(1931)561.

[2] E.g. R. Becker and W. Döring, Ferromagnetismus (Springer-Verlag, Berlin 1939) p. 270ff.

[3] V. for instance: J. H. Van Vleck, Phys. Rev. **52**(1937)1178; C. Kittel, Rev. Mod. Phys. **21**(1949)541.

APPENDIX I

The Hamilton operator for a set of composite particles with spin

The Hamilton operator for a set of nuclei and electrons with spin in the c^{-2} approximation has been given in (IX.37). We introduce new canonical variables with the help of the transformation formulae (VII.A45) and (VII.A46). (Here the non-relativistic central point $\boldsymbol{R}_k$ is employed, not the central point $\boldsymbol{X}_k$, since the latter is not a canonical variable.) The Weyl transform of the Hamilton operator then becomes

$$
\begin{aligned}
H_{\mathrm{op}}(1, \ldots, N; t) \rightleftarrows & \sum_k \left\{ \frac{\boldsymbol{P}_k^2}{2m_k} + \sum_{i=1}^{f-1} \frac{\boldsymbol{p}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{\boldsymbol{p}_{ki}\cdot\boldsymbol{p}_{kj}}{2m_k} - c^{-2} \sum_i \frac{\boldsymbol{P}_{ki}^4(\boldsymbol{p})}{8m_{ki}^3} \right\} \\
& + \sum_{ki,lj(ki\neq lj)} \frac{e_{ki}e_{lj}}{8\pi|\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})|} \left[1 - \frac{\boldsymbol{P}_{ki}(\boldsymbol{p})\cdot\mathrm{T}\{\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})\}\cdot\boldsymbol{P}_{lj}(\boldsymbol{p})}{2m_{ki}m_{lj}c^2}\right] \\
& + \sum_{ki,lj(ki\neq lj)}{}' \frac{e_{ki}e_{lj}\hbar}{4m_{ki}c^2} \left[\left\{\frac{\boldsymbol{P}_{ki}(\boldsymbol{p})}{m_{ki}} \wedge \boldsymbol{\sigma}_{ki}\right\}\cdot\nabla_{ki} - 2\left\{\frac{\boldsymbol{P}_{lj}(\boldsymbol{p})}{m_{lj}} \wedge \boldsymbol{\sigma}_{ki}\right\}\cdot\nabla_{ki}\right] \\
& \qquad \frac{1}{4\pi|\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})|} \\
& + \sum_{ki,lj(ki\neq lj)}{}'' \frac{e_{ki}e_{lj}\hbar^2}{8m_{ki}m_{lj}c^2} (\boldsymbol{\sigma}_{ki}\wedge\nabla_{ki})\cdot(\boldsymbol{\sigma}_{lj}\wedge\nabla_{ki}) \frac{1}{4\pi|\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})|} \\
& - \sum_{ki,lj(ki\neq lj)}{}' \frac{e_{ki}e_{lj}\hbar^2}{8m_{ki}^2c^2} \delta(\boldsymbol{R}_{ki}-\boldsymbol{R}_{lj}) + H_{\mathrm{e}}(1, \ldots, N; t).
\end{aligned} \tag{A1}
$$

The symbols $\boldsymbol{P}_{ki}(\boldsymbol{p})$ and $\boldsymbol{R}_{ki}(\boldsymbol{q})$ stand for the right-hand sides of (VII.A46). The quantity $H_{\mathrm{e}}(1, \ldots, N; t)$ represents the external field terms in (IX.37). If the external potentials are expanded around $\boldsymbol{R}_k$ and only first derivatives are retained, one gets

$$
\begin{aligned}
H_{\mathrm{e}}(1, \ldots, N; t) = & \sum_k e_k \left\{\varphi_{\mathrm{e}}(\boldsymbol{R}_k, t) - c^{-1}\frac{\boldsymbol{P}_k}{m_k}\cdot\boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}_k, t)\right\} \\
& + \sum_{k,i} e_{ki} \left[\{\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_k\}\cdot\nabla_k \left\{\varphi_{\mathrm{e}}(\boldsymbol{R}_k, t) - c^{-1}\frac{\boldsymbol{P}_k}{m_k}\cdot\boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}_k, t)\right\}\right. \\
& - c^{-1}\left\{\frac{\boldsymbol{P}_{ki}(\boldsymbol{p})}{m_{ki}} - \frac{\boldsymbol{P}_k}{m_k}\right\}\cdot\boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}_k, t) \\
& \left. - c^{-1}\{\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_k\}\cdot\nabla_k\boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}_k, t)\cdot\left\{\frac{\boldsymbol{P}_{ki}(\boldsymbol{p})}{m_{ki}} - \frac{\boldsymbol{P}_k}{m_k}\right\}\right] \\
& - \sum_{k,i}{}' \frac{e_{ki}\hbar}{2m_{ki}c}\boldsymbol{\sigma}_{ki}\cdot\left\{\boldsymbol{B}_{\mathrm{e}}(\boldsymbol{R}_k, t) - \frac{\boldsymbol{P}_{ki}(\boldsymbol{p})}{2m_{ki}c}\wedge\boldsymbol{E}_{\mathrm{e}}(\boldsymbol{R}_k, t)\right\}.
\end{aligned} \tag{A2}
$$

A different form for the Weyl transform of the Hamilton operator is obtained, if one splits off the kinetic energy

$$
\sum_{k,i} \{\tfrac{1}{2}m_{ki}(\partial_{t\mathrm{P}}\boldsymbol{X}_{ki})^2 + \tfrac{3}{8}c^{-2}m_{ki}(\partial_{t\mathrm{P}}\boldsymbol{X}_{ki})^4\}, \tag{A3}
$$

which, according to the derivation of the energy law in chapter IX, section 6*b*, may be written in semi-relativistic approximation as:

$$
\begin{aligned}
\sum_k (\tfrac{1}{2}m_k\boldsymbol{v}_k^2 + t_k) + 2c^{-2} & \sum_{k,l(k\neq l)} \sum_{i,j} e_{ki}e_{lj}\boldsymbol{r}_{ki}\cdot\boldsymbol{v}_k(\partial_{t\mathrm{P}}\boldsymbol{r}_{ki})\cdot\nabla_{ki}\frac{1}{4\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj}|} \\
& - 2c^{-2}\sum_{k,i} e_{ki}\boldsymbol{r}_{ki}\cdot\boldsymbol{v}_k(\partial_{t\mathrm{P}}\boldsymbol{r}_{ki})\cdot\boldsymbol{E}_{\mathrm{e}}(\boldsymbol{X}_{ki}, t),
\end{aligned} \tag{A4}
$$

where we introduced the abbreviations $\boldsymbol{v}_k \equiv \partial_{t\mathrm{P}}\boldsymbol{X}_k$ and t_k (IX.82). The kinetic energy may be expressed in terms of the canonical variables introduced above. Then one finds for (A3) up to terms of order c^{-2} and bilinear in the charges:

$$
\begin{aligned}
\sum_{k,i} & \left\{\frac{\boldsymbol{P}_k^2}{2m_k} + \sum_{i=1}^{f-1}\frac{\boldsymbol{p}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1}\frac{\boldsymbol{p}_{ki}\cdot\boldsymbol{p}_{kj}}{2m_k} - c^{-2}\sum_i\frac{\boldsymbol{P}_{ki}^4(\boldsymbol{p})}{8m_{ki}^3}\right\} \\
& - \sum_{ki,lj(ki\neq lj)} \frac{e_{ki}e_{lj}\boldsymbol{P}_{ki}(\boldsymbol{p})\cdot\mathrm{T}\{\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})\}\cdot\boldsymbol{P}_{lj}(\boldsymbol{p})}{8\pi m_{ki}m_{lj}c^2|\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})|} \\
& - \sum_{ki,lj(ki\neq lj)}{}' \frac{e_{ki}e_{lj}\hbar}{2m_{ki}m_{lj}c^2}\{\boldsymbol{P}_{lj}(\boldsymbol{p})\wedge\boldsymbol{\sigma}_{ki}\}\cdot\nabla_{ki}\frac{1}{4\pi|\boldsymbol{R}_{ki}(\boldsymbol{q})-\boldsymbol{R}_{lj}(\boldsymbol{q})|} \\
& - c^{-1}\sum_{k,i} e_{ki}\boldsymbol{P}_{ki}(\boldsymbol{p})\cdot\boldsymbol{A}_{\mathrm{e}}\{\boldsymbol{R}_{ki}(\boldsymbol{q}), t\}.
\end{aligned} \tag{A5}
$$

By employing the identity that follows by equating the expressions (A4) and (A5) one finds for the Hamiltonian (A1) with (A2) in semi-relativistic approximation:

$$H_{\mathrm{op}}(1, \ldots, N; t) \rightleftarrows \sum_k (\tfrac{1}{2}m_k \boldsymbol{v}_k^2 + \boldsymbol{v}_k\cdot \boldsymbol{g}_k + t_k + u_k)$$
$$+ \sum_{k,l(k\neq l)} \sum_{i,j} \frac{e_{ki}e_{lj}}{8\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj}|} \{1+\tfrac{1}{2}c^{-2}(\partial_{t\mathrm{P}}\boldsymbol{X}_{ki})\cdot \mathsf{T}(\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj})\cdot(\partial_{t\mathrm{P}}\boldsymbol{X}_{lj})\}$$
$$+2c^{-2} \sum_{k,l(k\neq l)} \sum_{i,j} e_{ki}e_{lj}\boldsymbol{r}_{ki}\cdot \boldsymbol{v}_k(\partial_{t\mathrm{P}}\boldsymbol{r}_{ki})\cdot \boldsymbol{\nabla}_{ki} \frac{1}{4\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj}|}$$
$$+ \sum_{k,l(k\neq l)} \sum_{i,j}{}' \frac{e_{ki}e_{lj}\hbar}{2m_{ki}c^2}(\partial_{t\mathrm{P}}\boldsymbol{X}_{ki})\cdot(\boldsymbol{\sigma}_{ki}\wedge \boldsymbol{\nabla}_{ki}) \frac{1}{4\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj}|}$$
$$+ \sum_{k,l(k\neq l)} \sum_{i,j}{}'' \frac{e_{ki}e_{lj}\hbar^2}{8m_{ki}m_{lj}c^2}(\boldsymbol{\sigma}_{ki}\wedge \boldsymbol{\nabla}_{ki})\cdot(\boldsymbol{\sigma}_{lj}\wedge \boldsymbol{\nabla}_{ki}) \frac{1}{4\pi|\boldsymbol{X}_{ki}-\boldsymbol{X}_{lj}|}$$
$$+H_{\mathrm{e}}'(1, \ldots, N: t), \quad \text{(A6)}$$

where we introduced $\boldsymbol{X}_{ki}$ and $\partial_{t\mathrm{P}}\boldsymbol{X}_{ki}$ instead of $\boldsymbol{R}_{ki}$ and $\boldsymbol{P}_{ki}$ respectively and moreover the abbreviations $\boldsymbol{g}_k$ (IX.69) and u_k (IX.78). The external field terms represented by $H_{\mathrm{e}}'(1, \ldots, N; t)$, are found to be, upon Taylor expansion,

$$H_{\mathrm{e}}'(1, \ldots, N; t) = \sum_k e_k \varphi_{\mathrm{e}}(\boldsymbol{X}_k, t)$$
$$+ \sum_{k,i} e_{ki}\boldsymbol{r}_{ki}\cdot \boldsymbol{\nabla}_k \varphi_{\mathrm{e}}(\boldsymbol{X}_k, t) - \sum_{k,i}{}' \frac{e_{ki}\hbar}{2m_{ki}c}\boldsymbol{\sigma}_{ki}\cdot\{\boldsymbol{B}_{\mathrm{e}}(\boldsymbol{X}_k, t)$$
$$-c^{-1}(\partial_{t\mathrm{P}}\boldsymbol{X}_{ki})\wedge \boldsymbol{E}_{\mathrm{e}}(\boldsymbol{X}_k, t)\} - 2c^{-2}\sum_{k,i} e_{ki}\boldsymbol{r}_{ki}\cdot \boldsymbol{v}_k(\partial_{t\mathrm{P}}\boldsymbol{r}_{ki})\cdot \boldsymbol{E}_{\mathrm{e}}(\boldsymbol{X}_k, t), \quad \text{(A7)}$$

where only terms up to first derivatives of the potentials have been retained.

For uniform and time-independent external fields the potentials may be chosen as

$$\varphi_{\mathrm{e}}(\boldsymbol{R}) = -\boldsymbol{R}\cdot \boldsymbol{E}_{\mathrm{e}}, \qquad \boldsymbol{A}_{\mathrm{e}}(\boldsymbol{R}) = \tfrac{1}{2}\boldsymbol{B}_{\mathrm{e}}\wedge \boldsymbol{R}. \quad \text{(A8)}$$

Then the external field term $H_{\mathrm{e}}(1, \ldots, N; t)$ given by (A2) becomes

$$H_{\mathrm{e}}(1, \ldots, N; t) = -\sum_k \left\{ e_k \boldsymbol{R}_k\cdot \left(\boldsymbol{E}_{\mathrm{e}} + \tfrac{1}{2}c^{-1}\frac{\boldsymbol{P}_k}{m_k}\wedge \boldsymbol{B}_{\mathrm{e}}\right)\right.$$
$$+\bar{\boldsymbol{\mu}}_{k,\mathrm{orb}}^{(1)}\cdot \left(\boldsymbol{E}_{\mathrm{e}} + \tfrac{1}{2}c^{-1}\frac{\boldsymbol{P}_k}{m_k}\wedge \boldsymbol{B}_{\mathrm{e}}\right) + \tfrac{1}{2}c^{-1}(\partial_{t\mathrm{P}}\boldsymbol{\mu}_{k,\mathrm{orb}}^{(1)})\cdot(\boldsymbol{B}_{\mathrm{e}}\wedge \boldsymbol{R}_k)$$
$$\left. +\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\cdot \boldsymbol{B}_{\mathrm{e}} + \boldsymbol{v}_{k,\mathrm{spin}}^{(1)}\cdot \left(\boldsymbol{B}_{\mathrm{e}} - \tfrac{1}{2}c^{-1}\frac{\boldsymbol{P}_k}{m_k}\wedge \boldsymbol{E}_{\mathrm{e}}\right) + \tfrac{1}{2}\boldsymbol{\mu}_{k,\mathrm{spin}}^{(1)}\cdot \boldsymbol{E}_{\mathrm{e}}\right\}. \quad \text{(A9)}$$

Here we introduced the electric and magnetic orbital and spin dipole moments, defined in (IX.65) with the choice $\boldsymbol{X}_k$ for the privileged point. In the first instance we encounter here dipole moments containing $\boldsymbol{R}_{ki}$ and $\boldsymbol{R}_k$, i.e.

dipole moments such as defined in non-relativistic theory and denoted by a bar. Since however the difference between $\boldsymbol{X}_{ki}$ and $\boldsymbol{R}_{ki}$ (and hence between $\boldsymbol{X}_k$ and $\boldsymbol{R}_k$) is of order c^{-2}, it follows by inspection of the various terms in (A9) and of the definitions (IX.65) that the difference between the two kinds of multipole moments is significant only in the second term of $H_{\mathrm{e}}(1, \ldots, N; t)$. The orbital electric dipole moment $\bar{\boldsymbol{\mu}}_{k,\mathrm{orb}}^{(1)}$ which is defined as $\sum_i e_{ki}(\boldsymbol{R}_{ki}-\boldsymbol{R}_k)$ may be related to the semi-relativistic dipole moments. For the case of neutral atoms ($e_k = 0$) one finds from (IX.65) with (IX.38, 61) in semi-relativistic approximation:

$$\bar{\boldsymbol{\mu}}_{k,\mathrm{orb}}^{(1)} = \boldsymbol{\mu}_{k,\mathrm{orb}}^{(1)} + \tfrac{1}{2}\boldsymbol{\mu}_{k,\mathrm{spin}}^{(1)} - c^{-1}(\boldsymbol{v}_{k,\mathrm{orb}}^{(1)} + \tfrac{1}{2}\boldsymbol{v}_{k,\mathrm{spin}}^{(1)})\wedge \frac{\boldsymbol{P}_k}{m_k}. \quad \text{(A10)}$$

The term $H_{\mathrm{e}}'(1, \ldots, N; t)$ that is given in (A7) may likewise be written in a different way, if one introduces the potentials (A8) and the multipoles (IX.65). One finds then

$$H_{\mathrm{e}}'(1, \ldots, N; t) = -\sum_k \{e_k \boldsymbol{X}_k\cdot \boldsymbol{E}_{\mathrm{e}} + (\boldsymbol{\mu}_k^{(1)} - c^{-1}\boldsymbol{v}_k^{(1)}\wedge \boldsymbol{v}_k)\cdot \boldsymbol{E}_{\mathrm{e}}$$
$$+\boldsymbol{v}_{k,\mathrm{spin}}^{(1)}\cdot \boldsymbol{B}_{\mathrm{e}} + 2c^{-1}(\boldsymbol{v}_{k,\mathrm{orb}}^{(1)}\wedge \boldsymbol{v}_k)\cdot \boldsymbol{E}_{\mathrm{e}}\}. \quad \text{(A11)}$$

APPENDIX II

Change of free energy under deformations for a spin particle system

The free energy F^* follows from the partition sum (VII.A58). The Hamilton operator $H_{\mathrm{op}}^{\mathrm{W}}$ contains a wall potential $U_{\mathrm{op}}^{\mathrm{W}}$ that depends on the position of the boundary, so that it changes under deformations. The change of free energy is therefore given by (VII.A63) or, in terms of the Wigner function of the canonical ensemble and the Weyl transform U^{W} of the wall potential, by

$$\delta_\varepsilon F^* = \mathrm{Sp}\int \delta U^{\mathrm{W}} \rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N. \qquad \text{(A12)}$$

The wall potential is a sum of functions U_k^{W} which depend on $\boldsymbol{X}_k$ given in (IX.68) with (IX.38, 39). It is to be understood in the same fashion as for instance (IX.47):

$$U^{\mathrm{W}} = \sum_k U_k^{\mathrm{W}}(\boldsymbol{X}_k) \equiv \sum_k \{U_k^{\mathrm{W}}(\boldsymbol{R}_k) + (\boldsymbol{X}_k - \boldsymbol{R}_k)\cdot\nabla_k U_k^{\mathrm{W}}(\boldsymbol{R}_k)\}, \qquad \text{(A13)}$$

where $\boldsymbol{X}_k - \boldsymbol{R}_k$ is of the order c^{-2}. The wall potential $U_k^{\mathrm{W}}(\boldsymbol{R}_k)$ is a function which is zero if $\boldsymbol{R}_k$ is situated in the interior of the system, increases rapidly at the position of the wall and becomes infinite outside.

If the position of the wall changes according to (VII.A60), one may use as a new partial wall potential $U_k^{\mathrm{W}'}(\boldsymbol{R}_k)$ the old wall potential U_k^{W} with argument $\{\mathsf{U} - \delta\boldsymbol{\epsilon}(\boldsymbol{R}_k)\}\cdot\boldsymbol{R}_k$, as in (VII.A61). Then the new wall potential $U^{\mathrm{W}'}$ is

$$U^{\mathrm{W}'} = \sum_k U_k^{\mathrm{W}}[\{\mathsf{U} - \delta\boldsymbol{\epsilon}(\boldsymbol{R}_k)\}\cdot\boldsymbol{R}_k] + \sum_k (\boldsymbol{X}_k - \boldsymbol{R}_k)\cdot\nabla_k U_k^{\mathrm{W}}[\{\mathsf{U} - \delta\boldsymbol{\epsilon}(\boldsymbol{R}_k)\}\cdot\boldsymbol{R}_k]. \qquad \text{(A14)}$$

Hence the change of the wall potential is

$$\delta U^{\mathrm{W}} = -\sum_k [\boldsymbol{R}_k\cdot\delta\tilde{\boldsymbol{\epsilon}}(\boldsymbol{R}_k)\cdot\nabla_k U_k^{\mathrm{W}}(\boldsymbol{R}_k) + (\boldsymbol{X}_k - \boldsymbol{R}_k)\cdot\nabla_k\{\boldsymbol{R}_k\cdot\delta\tilde{\boldsymbol{\epsilon}}(\boldsymbol{R}_k)\cdot\nabla_k U_k^{\mathrm{W}}(\boldsymbol{R}_k)\}] \qquad \text{(A15)}$$

or, performing the differentiation in the second term,

$$\delta U^{\mathrm{W}} = -\sum_k \boldsymbol{X}_k\cdot\delta\tilde{\boldsymbol{\epsilon}}(\boldsymbol{X}_k)\cdot\nabla_k U_k^{\mathrm{W}}(\boldsymbol{X}_k) \qquad \text{(A16)}$$

up to order c^{-2}. Substituting this result into (A12) one gets for the change of

the free energy:

$$\delta_\varepsilon F^* = -\mathrm{Sp}\int \{\sum_k \boldsymbol{X}_k\cdot\delta\tilde{\boldsymbol{\epsilon}}(\boldsymbol{X}_k)\cdot\nabla_k U_k^{\mathrm{W}}(\boldsymbol{X}_k)\}\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N. \qquad \text{(A17)}$$

This expression bears a strong similarity to the non-relativistic form (VII. A65), the sole difference being that $\boldsymbol{R}_k$ is replaced by $\boldsymbol{X}_k$ (and a spur added since the Wigner function and the quantity in front of it are matrices).

To bring the right-hand side of (A17) into a more convenient form, we proceed in a way analogous to that followed in non-relativistic theory. Since the canonical ensemble is stationary, one has the identity

$$0 = \frac{\partial}{\partial t}\mathrm{Sp}\int \sum_k \boldsymbol{P}_k\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k\,\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N, \qquad \text{(A18)}$$

because the Wigner function is time-independent. With the use of the relation (9) one may write this identity in semi-relativistic approximation as:

$$0 = \mathrm{Sp}\int \sum_k \partial_{t\mathrm{P}}\{\boldsymbol{P}_k\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k\}\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N$$
$$-\mathrm{Sp}\int \sum_k \Big[(\nabla_k U^{\mathrm{W}})\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k + \frac{1}{m_k^2 c^2}\{(\sum_i \tfrac{1}{2}\hbar\boldsymbol{\sigma}_{ki})\wedge\nabla_k U^{\mathrm{W}}\}\cdot\nabla_k$$
$$\{\boldsymbol{P}_k\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k\}\Big]\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N. \qquad \text{(A19)}$$

The first term contains the Poisson bracket of $\sum_k \boldsymbol{P}_k\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k$ with the Weyl transform of the Hamilton operator without wall potential, while the second comes about as a result of the wall potential part of the total Hamiltonian. It contains the force $-\nabla_k U^{\mathrm{W}}$, which the wall exerts on atom k. Combining (A17) and (A19) we find for the change of the free energy under deformation

$$\delta_\varepsilon F^* = -\mathrm{Sp}\int \sum_k \partial_{t\mathrm{P}}\{\boldsymbol{P}_k\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k\}\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N$$
$$+\mathrm{Sp}\int \sum_k \frac{1}{m_k^2 c^2}\{(\sum_i \tfrac{1}{2}\hbar\boldsymbol{\sigma}_{ki})\wedge(\nabla_k U^{\mathrm{W}})\}\cdot\nabla_k\{\boldsymbol{P}_k\cdot\delta\boldsymbol{\epsilon}(\boldsymbol{X}_k)\cdot\boldsymbol{X}_k\}$$
$$\rho(1, \ldots, N)\mathrm{d}1 \ldots \mathrm{d}N. \qquad \text{(A20)}$$

This result may be compared to (VII.A68) with (II.A51) of the non-relativistic theory. In the first place the central point $\boldsymbol{X}_k$ instead of $\boldsymbol{R}_k$ appears. Furthermore a second term occurs here in the expression for $\delta_\varepsilon F^*$. However this term is proportional to the surface of the system, since the order of magnitude of the factor of $\delta\boldsymbol{\epsilon}$ can be estimated by writing the product of the Compton wave length $\hbar/m_k c$ of the composite particle, the pressure times the surface of the walls and c^{-1} times the average velocity $(\sim \boldsymbol{P}_k/m_k)$ of the composite particles. The first term of (A20) is proportional to the volume of the system as is shown in section 5*b* of this chapter. Since in the thermodynamical treatment given here surface effects have been neglected throughout, one may write for (A20):

$$\delta_\varepsilon F^* = -\mathrm{Sp} \int \sum_k \partial_{t\mathrm{P}} \{\boldsymbol{P}_k \cdot \delta\boldsymbol{\epsilon}(\boldsymbol{X}_k) \cdot \boldsymbol{X}_k\} \rho(1, \ldots, N) \mathrm{d}1 \ldots \mathrm{d}N. \qquad \text{(A21)}$$

In the case of uniform deformations $\delta\boldsymbol{\epsilon}$ one finds from this expression

$$\delta_\varepsilon F^* = \mathbf{A} : \delta\boldsymbol{\epsilon} \qquad \text{(A22)}$$

with the tensor

$$\mathbf{A} \equiv -\mathrm{Sp} \int \sum_k \partial_{t\mathrm{P}} (\boldsymbol{X}_k \boldsymbol{P}_k) \rho(1, \ldots, N) \mathrm{d}1 \ldots \mathrm{d}N, \qquad \text{(A23)}$$

which is the expression (89) of the main text.