

Quantum statistical description of material media

1 Introduction

Macroscopic laws are obtained from laws at the atomic level by means of an appropriate averaging procedure. Since the atomic laws were formulated in terms of Weyl transforms, such an averaging will involve the use of Wigner functions for statistical, i.e. mixed states. In deriving the macroscopic laws in this way we take full advantage of the close analogy with classical theory. It will then turn out that the macroscopic quantum-mechanical laws obtained have the same form as the classical laws. The macroscopic quantities are also to a great extent analogous: most of them may be obtained from the classical quantities by replacing the distribution functions by Wigner functions.

2 The Wigner function in statistical mechanics

In quantum statistics a system is described by a density operator¹ P , which corresponds to a mixed state:

$$P(t) = \sum_{\gamma} w_{\gamma} |\psi_{\gamma}(t)\rangle \langle \psi_{\gamma}(t)| \quad (1)$$

with weights w_{γ} , normalized to unity,

$$\sum_{\gamma} w_{\gamma} = 1 \quad (2)$$

and pure state vectors $|\psi_{\gamma}(t)\rangle$ that form a complete orthonormal set. Average values of physical quantities, represented by operators A , are given by

$$\bar{A} = \sum_{\gamma} w_{\gamma} \langle \psi_{\gamma} | A | \psi_{\gamma} \rangle = \text{Tr}(PA). \quad (3)$$

¹ In this section, as in section 3 of chapter VI, we use capitals for operators and lower case symbols for Weyl transforms.

Since in the preceding we used Weyl transforms rather than operators to represent physical quantities, we want to express also the average values (3) with the help of Weyl transforms. To that end we introduce the Wigner function as the Weyl transform (times h^3) of the density operator (1). Then one finds

$$\rho(\mathbf{p}, \mathbf{q}; t) = \sum_{\gamma} w_{\gamma} \rho_{\gamma}(\mathbf{p}, \mathbf{q}; t) \quad (4)$$

with the partial Wigner functions $\rho_{\gamma}(\mathbf{p}, \mathbf{q}; t)$ for pure states defined as (VI.54) in chapter VI, section 3b:

$$\rho_{\gamma}(\mathbf{p}, \mathbf{q}; t) = h^{-3} \int d\mathbf{v} e^{(i/\hbar)\mathbf{p}\cdot\mathbf{v}} \psi_{\gamma}(\mathbf{q} - \frac{1}{2}\mathbf{v}; t) \psi_{\gamma}^*(\mathbf{q} + \frac{1}{2}\mathbf{v}; t), \quad (5)$$

where $\psi_{\gamma}(\mathbf{q}; t)$ is the wave function of the pure state $|\psi_{\gamma}\rangle$.

With the help of this Wigner function (4) one may write the average (3) as

$$\bar{A} = \bar{a}, \quad (6)$$

where the right-hand side is the integral:

$$\bar{a} \equiv \int d\mathbf{p} d\mathbf{q} a(\mathbf{p}, \mathbf{q}) \rho(\mathbf{p}, \mathbf{q}; t), \quad (7)$$

as follows from (VI.51–52). Introducing (4) one may write (6) with (7) alternatively as

$$\bar{A} = \sum_{\gamma} w_{\gamma} \bar{a}^{\gamma} \quad (8)$$

with the pure state integral

$$\bar{a}^{\gamma} \equiv \int d\mathbf{p} d\mathbf{q} a(\mathbf{p}, \mathbf{q}) \rho_{\gamma}(\mathbf{p}, \mathbf{q}; t). \quad (9)$$

From the normalization of the partial Wigner functions (VI.56) and formula (2) it follows that also the total Wigner function (4) is normalized:

$$\int d\mathbf{p} d\mathbf{q} \rho(\mathbf{p}, \mathbf{q}; t) = 1. \quad (10)$$

Just as the partial Wigner functions for pure states, the total Wigner function introduced here cannot be interpreted as a probability density in phase space. The integrals over the momenta (or over the coordinates) however are positive definite and may be interpreted as probability densities:

$$\int d\mathbf{p} \rho(\mathbf{p}, \mathbf{q}; t) = \sum_{\gamma} w_{\gamma} |\psi_{\gamma}(\mathbf{q})|^2 \geq 0. \quad (11)$$

The time evolution of the Wigner function follows from the time evolution of the partial Wigner functions, given in (VI.59). As a result one gets an equation

$$\frac{\partial \rho(\mathbf{p}, \mathbf{q}; t)}{\partial t} = \frac{2}{\hbar} \sin \left\{ \frac{\hbar}{2} \left(\frac{\partial^{(h)}}{\partial \mathbf{q}} \cdot \frac{\partial^{(\rho)}}{\partial \mathbf{p}} - \frac{\partial^{(h)}}{\partial \mathbf{p}} \cdot \frac{\partial^{(\rho)}}{\partial \mathbf{q}} \right) \right\} h(\mathbf{p}, \mathbf{q}) \rho(\mathbf{p}, \mathbf{q}; t), \quad (12)$$

which has the same form as (VI.59). From this equation one finds an expression for the time derivative of an average quantity (6):

$$\frac{d\bar{a}(t)}{dt} = \frac{2}{\hbar} \int d\mathbf{p} d\mathbf{q} \left[\sin \left\{ \frac{\hbar}{2} \left(\frac{\partial^{(a)}}{\partial \mathbf{q}} \cdot \frac{\partial^{(h)}}{\partial \mathbf{p}} - \frac{\partial^{(a)}}{\partial \mathbf{p}} \cdot \frac{\partial^{(h)}}{\partial \mathbf{q}} \right) \right\} a(\mathbf{p}, \mathbf{q}) h(\mathbf{p}, \mathbf{q}) \right] \rho(\mathbf{p}, \mathbf{q}; t), \quad (13)$$

formally the same as (VI.60).

For many-particle systems the averages of physical quantities can also be obtained with the help of the Weyl transforms of the operators corresponding to these quantities, and Wigner functions. Both the Weyl transform and the Wigner function depend then on the phase space variables of all particles.

3 Reduced Wigner functions

The formalism outlined in the preceding section will be applied to systems of N atoms, labelled by $k = 1, 2, \dots, N$, that consist of a number of point particles, labelled by k, i . Then the Weyl transform of the operator corresponding to a physical quantity will depend on all momentum and coordinate variables¹ $\mathbf{P}_{ki}, \mathbf{R}_{ki}$ ($k = 1, 2, \dots, N; i = 1, 2, \dots$) of the particles. The total set of variables will for short be denoted $1, 2, \dots, N$.

Often the operators pertinent to physical quantities are sums of operators which depend on the variables of one single atom only, i.e. which are of the form

$$a_{\text{op}} = \sum_k a_{k,\text{op}}. \quad (14)$$

Here the quantities $a_{k,\text{op}}$ depend on the coordinate and momentum operators $\mathbf{P}_{ki,\text{op}}$ and $\mathbf{R}_{ki,\text{op}}$ of the constituent particles $i = 1, 2, \dots$ of atom k . The Weyl transform of such a quantity is equal to

$$a_{\text{op}} \rightleftharpoons a(1, \dots, N) = \sum_k a_k(k), \quad (15)$$

where k indicates all momentum and coordinate variables of atom k .

¹ We now return to the notation according to which operators are distinguished by a label op and quantities without such a label indicate ordinary numbers.

If the system consists of identical atoms the average (7) of the quantity (15) may be written as:

$$\bar{a} = N \int a_1(1) \rho(1, 2, \dots, N; t) d1 \dots dN, \quad (16)$$

or alternatively as:

$$\bar{a} = \int a_1(1) f_1(1; t) d1, \quad (17)$$

where the reduced Wigner function defined as

$$f_1(1; t) \equiv N \int \rho(1, 2, \dots, N; t) d2 \dots dN \quad (18)$$

is a one-point function, normalized to N . In practice it is often convenient to introduce instead of the momentum and coordinate variables \mathbf{P}_{1i} and \mathbf{R}_{1i} ($i = 1, 2, \dots$) different variables in the integral (17). The Jacobian of such a transformation may then for convenience be absorbed in the new one-point function. For formal reasons one may then maintain the notation $f_1(1; t)$.

Furthermore one encounters two-point operators, which have Weyl transforms

$$a_{\text{op}} \rightleftharpoons a(1, \dots, N) = \sum_{k,l(k \neq l)} a_{kl}(k, l). \quad (19)$$

Then (7) leads to the average value

$$\bar{a} = \int a_{12}(1, 2) f_2(1, 2; t) d1 d2, \quad (20)$$

where the reduced Wigner function

$$f_2(1, 2; t) \equiv N(N-1) \int \rho(1, 2, \dots, N; t) d3 \dots dN \quad (21)$$

is a two-point function normalized to $N(N-1)$.

In contrast to the distribution functions of classical theory the one-point and two-point Wigner functions do not admit an interpretation in terms of probabilities. However such an interpretation is possible if one integrates away either all momentum or all coordinate variables.

In the following we want to have at our disposal also two-point 'correlation functions', which are defined as

$$c_2(1, 2; t) \equiv f_2(1, 2; t) - f_1(1; t) f_1(2; t). \quad (22)$$

For mixtures of several chemical components one needs an extra index to

label the reduced one- and two-component distribution functions for the various species.

4 The Maxwell equations

The starting point for the derivation of the Maxwell equations is the set of equations (VI.90) for the expectation values of the operators representing the atomic fields.

In the set of equations (VI.90) all symbols denote in fact pure state integrals of the type (9). By making a weighted sum of these equations we get according to (3), or (8) with (9), the equations for average quantities

$$\begin{aligned} \nabla \cdot \mathbf{E} &= \varrho^e - \nabla \cdot \mathbf{P}, \\ -\partial_0 \mathbf{E} + \nabla \wedge \mathbf{B} &= c^{-1} \mathbf{J} + \partial_0 \mathbf{P} + \nabla \wedge \mathbf{M}, \\ \nabla \cdot \mathbf{B} &= 0, \\ \partial_0 \mathbf{B} + \nabla \wedge \mathbf{E} &= 0, \end{aligned} \quad (23)$$

where the macroscopic fields are defined as

$$\begin{aligned} \mathbf{E}(\mathbf{R}, t) &= \int \mathbf{e}(1, \dots, N; \mathbf{R}, t) \rho(1, \dots, N; t) d1 \dots dN = \sum_{\gamma} w_{\gamma} \bar{\mathbf{e}}^{\gamma}, \\ \mathbf{B}(\mathbf{R}, t) &= \int \mathbf{b}(1, \dots, N; \mathbf{R}, t) \rho(1, \dots, N; t) d1 \dots dN = \sum_{\gamma} w_{\gamma} \bar{\mathbf{b}}^{\gamma}. \end{aligned} \quad (24)$$

Furthermore the macroscopic charge and current densities are given by:

$$\begin{aligned} \varrho^e(\mathbf{R}, t) &= \int \rho^e(1, \dots, N; \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN = \sum_{\gamma} w_{\gamma} \bar{\rho}^{\gamma}, \\ \mathbf{J}(\mathbf{R}, t) &= \int \mathbf{j}(1, \dots, N; \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN = \sum_{\gamma} w_{\gamma} \bar{\mathbf{j}}^{\gamma}. \end{aligned} \quad (25)$$

Inserting (VI.85) and introducing the one-point reduced Wigner function (18) we may write these expressions as (cf. (II.19)):

$$\begin{aligned} \varrho^e(\mathbf{R}, t) &= \sum_a e_a f_1^a(\mathbf{R}; t), \\ \mathbf{J}(\mathbf{R}, t) &= \sum_a \int e_a \mathbf{v}_1 f_1^a(\mathbf{R}, \mathbf{v}_1; t) d\mathbf{v}_1, \end{aligned} \quad (26)$$

where a labels the various species in the system.

The macroscopic polarization densities are defined as:

$$P(\mathbf{R}, t) = \int p(1, \dots, N; \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN = \sum_{\gamma} w_{\gamma} \bar{p}^{\gamma}, \quad (27)$$

$$M(\mathbf{R}, t) = \int \mathbf{m}(1, \dots, N; \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN = \sum_{\gamma} w_{\gamma} \bar{\mathbf{m}}^{\gamma},$$

or with (VI.86) and the one-point reduced Wigner function (18) (cf. (II.21)) as:

$$P(\mathbf{R}, t) = \sum_a \sum_{n=1}^{\infty} (-1)^{n-1} \nabla^{n-1} : \int \bar{\mu}_1^{(n)} f_1^a(\mathbf{R}, 1; t) d1, \quad (28)$$

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

where $\beta_1 \equiv \mathbf{v}_1/c$.

In this way the Maxwell equations have been obtained in the framework of non-relativistic quantum mechanics. The macroscopic quantities are written as averages in terms of the Wigner function and Weyl transforms of operators on the atomic level. In particular the sources of the field equations contain the charge, current and polarization densities, given in (26) and (28) as expressions of the same form as the corresponding classical ones, but with one-point Wigner functions instead of one-point classical distribution functions. (The atomic operators of which these macroscopic quantities are the averages have been given in formulae (VI.91) and (VI.93) of the preceding chapter.)

As a consequence of the formal similarity of the classical and quantum-mechanical results of the non-relativistic treatments, one may also take over the applications to particular media which were given in chapter II, again replacing the classical distribution functions by Wigner functions.

The proof of the validity of the macroscopic Maxwell equations has been given here for the case of non-relativistic particles and fields, i.e. both described by expressions up to order c^{-1} . In chapter III it was shown that taking the non-relativistic limit of the fields meant that one confined oneself to situations in which two dimensionless parameters are small: the ratio β of the source velocity to the velocity of light and the ratio of the retardation time to a characteristic time of the motion of the accelerated source. Sometimes however one is interested in an approximation in which only the source velocity is small, but not the retardation time. To derive the Maxwell equations in that case one must perform a second quantization of the fields¹.

¹ W. E. Brittin, Phys. Rev. **106**(1957)843; K. Schram, Physica **26**(1960)1080; J. M. Crowther and D. ter Haar, Proc. Kon. Ned. Akad. Wet. **B74**(1971)341, 351.

5 The momentum and energy equations

a. Introduction

The macroscopic balance equations and conservation laws of momentum and energy will be derived from the atomic equation of motion and the atomic energy equation by using an averaging procedure involving a Wigner function. The use of the latter function simplifies again the calculations considerably in the sense that many derivations of classical theory can be taken over. The results of the present quantum-mechanical treatment will differ slightly more from classical theory than those of the preceding section where only the classical distribution functions had to be replaced by Wigner functions.

Just as in classical theory it will be convenient to derive the mass conservation law before turning to the momentum and energy equations. The treatment will be confined to one-component systems.

b. The mass conservation law

The operator for the mass density on the atomic level has the form

$$\sum_k m_k \delta(\mathbf{R}_{k,op} - \mathbf{R}), \quad (29)$$

where $m_k = m$ is the mass of the identical atoms and where $\mathbf{R}_{k,op}$ is the mass centre operator $\sum_i m_{ki} \mathbf{R}_{ki,op} / m_k$. Its Weyl transform is

$$\sum_k m_k \delta(\mathbf{R}_k - \mathbf{R}). \quad (30)$$

By taking the Poisson bracket with the Weyl transform of the Hamiltonian one finds with the notation (VI.72)

$$\partial_{tP} \sum_k m_k \delta(\mathbf{R}_k - \mathbf{R}) = - \sum_k m_k (\partial_{tP} \mathbf{R}_k) \cdot \nabla \delta(\mathbf{R}_k - \mathbf{R}). \quad (31)$$

By multiplication with a Wigner function and integration over phase space one finds

$$\begin{aligned} \frac{\partial}{\partial t} \int \sum_k m_k \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ = - \nabla \cdot \int \sum_k m_k \mathbf{v}_k \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN, \end{aligned} \quad (32)$$

where we used (VI.61), (VI.72), (13) and the abbreviation $\mathbf{v}_k \equiv \partial_{tP} \mathbf{R}_k$.

With the introduction of reduced Wigner functions of the type (18), one may write (32) as

$$\frac{\partial \varrho}{\partial t} = -\mathbf{V} \cdot (\varrho \mathbf{v}) \quad (33)$$

with the macroscopic mass density

$$\varrho = m f_1(\mathbf{R}; t) \quad (34)$$

and the macroscopic mass flow

$$\varrho \mathbf{v} = \int m \mathbf{v}_1 f_1(\mathbf{R}, \mathbf{v}_1; t) d\mathbf{v}_1. \quad (35)$$

The macroscopic mass density is the average of the atomic operator (29), while the macroscopic mass flow is the average of the operator

$$\frac{1}{2} \sum_k m \{ \mathbf{v}_{k, \text{op}}, \delta(\mathbf{R}_{k, \text{op}} - \mathbf{R}) \}, \quad (36)$$

where $\mathbf{v}_{k, \text{op}}$ is defined in (VI.92) and where an anticommutator appears.

c. The momentum balance

The macroscopic momentum balance is obtained by multiplying the atomic equation of motion in its form (VI.98) by a delta function $\delta(\mathbf{R}_k - \mathbf{R})$, summing over k , multiplying by a Wigner function and integrating over phase space. Then one obtains

$$\begin{aligned} & \int \sum_k m_k (\partial_{t\mathbf{P}} \mathbf{v}_k) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ &= \int \sum_k (f_k^L + f_k^S) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \end{aligned} \quad (37)$$

The left-hand side may be brought into relation with the time derivative of the mass flow, which is

$$\frac{\partial(\varrho \mathbf{v})}{\partial t} = \frac{\partial}{\partial t} \int \sum_k m_k \mathbf{v}_k \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \quad (38)$$

With the help of (13) and (VI.61) one finds with the notation (VI.72)

$$\frac{\partial(\varrho \mathbf{v})}{\partial t} = \int \sum_k m_k \partial_{t\mathbf{P}} \{ \mathbf{v}_k \delta(\mathbf{R}_k - \mathbf{R}) \} \rho(1, \dots, N; t) d1 \dots dN. \quad (39)$$

If one carries out the differentiations at the right-hand side this equation becomes

$$\begin{aligned} \frac{\partial(\varrho \mathbf{v})}{\partial t} &= \int \sum_k m_k (\partial_{t\mathbf{P}} \mathbf{v}_k) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ &\quad - \mathbf{V} \cdot \int \sum_k m_k \mathbf{v}_k \mathbf{v}_k \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN, \end{aligned} \quad (40)$$

so that (37) may be written in the form

$$\begin{aligned} \frac{\partial(\varrho \mathbf{v})}{\partial t} &= -\mathbf{V} \cdot \int \sum_k m_k \mathbf{v}_k \mathbf{v}_k \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ &\quad + \int \sum_k (f_k^L + f_k^S) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \end{aligned} \quad (41)$$

Splitting the Weyl transform \mathbf{v}_k of the atomic velocity into the bulk velocity $\mathbf{v}(\mathbf{R}, t)$, defined by (35) with (34), and a fluctuation term $\hat{\mathbf{v}}_k$:

$$\mathbf{v}_k = \mathbf{v}(\mathbf{R}, t) + \hat{\mathbf{v}}_k(\mathbf{R}, t) \quad (42)$$

and introducing reduced Wigner functions of the type (18), one finds as the momentum balance

$$\frac{\partial(\varrho \mathbf{v})}{\partial t} = -\mathbf{V} \cdot (\varrho \mathbf{v} \mathbf{v} + \mathbf{P}^K) + \mathbf{F}^L + \mathbf{F}^S, \quad (43)$$

where we introduced a kinetic pressure tensor

$$\mathbf{P}^K = \int m \hat{\mathbf{v}}_1 \hat{\mathbf{v}}_1 f_1(\mathbf{R}, \mathbf{v}_1; t) d\mathbf{v}_1 \quad (44)$$

and the abbreviations for the long range and short range force densities

$$\mathbf{F}^{L,S} = \int \sum_k f_k^{L,S} \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \quad (45)$$

These expressions contain the atomic quantities (VI.99) and (VI.100), which have the same form as (I.54) and (I.52). For that reason we may take over the result of the classical evaluation of \mathbf{F}^L and \mathbf{F}^S . The only step which we should investigate is the one which involves the expression

$$c^{-1} \int \sum_k \partial_{t\mathbf{P}} \{ \bar{\mu}_k^{(1)} \wedge \mathbf{B}_c(\mathbf{R}_k, t) \} \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \quad (46)$$

(cf. the last term of (II.66)). Application of the relation (13) with the Weyl

transform (VI.61) of the Hamiltonian leads to the identity

$$\begin{aligned} & c^{-1} \int_k \partial_{tP} \{ \bar{\mu}_k^{(1)} \wedge \mathbf{B}_e(\mathbf{R}_k, t) \} \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ &= c^{-1} \frac{\partial}{\partial t} \int_k \bar{\mu}_k^{(1)} \wedge \mathbf{B}_e(\mathbf{R}_k, t) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ &+ c^{-1} \nabla \cdot \int_k \mathbf{v}_k \bar{\mu}_k^{(1)} \wedge \mathbf{B}_e(\mathbf{R}_k, t) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \quad (47) \end{aligned}$$

The right-hand side has the same form as the expression (II.67) of classical theory. This means that the long range force density, which occurs in (43), has the same form as (II.72):

$$\begin{aligned} \mathbf{F}^L &= q^\circ \mathbf{E} + c^{-1} \mathbf{J} \wedge \mathbf{B} + (\nabla \mathbf{E}) \cdot \mathbf{P} + (\nabla \mathbf{B}) \cdot \mathbf{M} \\ &+ c^{-1} \frac{\partial}{\partial t} (\mathbf{P} \wedge \mathbf{B}) + c^{-1} \nabla \cdot (\mathbf{v} \mathbf{P} \wedge \mathbf{B}) - \nabla \cdot \mathbf{P}^F + \mathbf{F}^C. \quad (48) \end{aligned}$$

The macroscopic Maxwell fields, charge-current and polarization densities are the quantum-mechanical averages (24), (26) and (28). The pressure \mathbf{P}^F and the correlation contribution \mathbf{F}^C to the long range force density are given by (II.73) and (II.74) where now f_1 and c_2 stand for the reduced Wigner functions (18) and (22).

Likewise the short range term \mathbf{F}^S in (43) is given by (II.75), where f_2 now stands for the two-point Wigner function (21).

The quantities that occur in the momentum equation have been given here as integrals over the product of Weyl transforms of certain operators and Wigner functions. The advantage of this way of writing resides in the fact that their form is as simple as the classical one. If one wishes one may write down the operators of the Weyl transforms that occur here. For instance one may find the operator of which the kinetic pressure (44) is the average by making use of (VI.31) and (VI.92). Then this operator turns out to be of the form

$$\frac{1}{4} \sum_k m_k \{ \mathbf{v}_{k,op} - \mathbf{v}(\mathbf{R}, t), \{ \mathbf{v}_{k,op} - \mathbf{v}(\mathbf{R}, t), \delta(\mathbf{R}_{k,op} - \mathbf{R}) \} \}, \quad (49)$$

involving a double anticommutator.

d. The energy balance

As in the derivation of the momentum law the macroscopic energy balance equation follows from the corresponding atomic equation (VI.105) by multi-

plication with the delta function $\delta(\mathbf{R}_k - \mathbf{R})$, summation over k , multiplication with a Wigner function and integration over the whole of phase space:

$$\begin{aligned} & \int_k \left[\partial_{tP} \left\{ \frac{1}{2} m_k \mathbf{v}_k^2 + \frac{1}{2} \sum_i m_{ki} (\partial_{tP} \mathbf{r}_{ki})^2 + \sum_{i,j(i \neq j)} \frac{e_{ki} e_{kj}}{8\pi |\mathbf{r}_{ki} - \mathbf{r}_{kj}|} \right\} \right] \\ & \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \\ &= \int_k (\psi_k^L + \psi_k^S) \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \quad (50) \end{aligned}$$

In order to rewrite the left-hand side we consider the following time derivative

$$\begin{aligned} & \frac{\partial}{\partial t} \int_k \left\{ \frac{1}{2} m_k \mathbf{v}_k^2 + \frac{1}{2} \sum_i m_{ki} (\partial_{tP} \mathbf{r}_{ki})^2 + \sum_{i,j(i \neq j)} \frac{e_{ki} e_{kj}}{8\pi |\mathbf{r}_{ki} - \mathbf{r}_{kj}|} \right\} \\ & \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN. \quad (51) \end{aligned}$$

This time derivative may be evaluated with the help of (13). Then one obtains, in view of the form (VI.61) of H , an integral over phase space with as integrand the product of the Wigner function $\rho(1, \dots, N; t)$ and the expression

$$\begin{aligned} & \left(\sum_{k,i} \left[\frac{\partial}{\partial \mathbf{R}_{ki}} \cdot \frac{\partial^{(H)}}{\partial \mathbf{P}_{ki}} \left\{ 1 - \frac{\hbar^2}{8} \left(\sum_{i,j} \frac{\partial}{\partial \mathbf{P}_{ij}} \cdot \frac{\partial^{(H)}}{\partial \mathbf{R}_{ij}} \right)^2 \right\} - \frac{\partial}{\partial \mathbf{P}_{ki}} \cdot \frac{\partial^{(H)}}{\partial \mathbf{R}_{ki}} \right] H(1, \dots, N; t) \right. \\ & \left. + \frac{\partial}{\partial t} \sum_m \left\{ \frac{1}{2} m_m \mathbf{v}_m^2 + \frac{1}{2} \sum_p m_{mp} (\partial_{tP} \mathbf{r}_{mp})^2 + \sum_{p,s(p \neq s)} \frac{e_{mp} e_{ms}}{8\pi |\mathbf{r}_{mp} - \mathbf{r}_{ms}|} \right\} \delta(\mathbf{R}_m - \mathbf{R}), \quad (52) \end{aligned}$$

where the differentiation symbols with label (H) act only on the Weyl transform H of the Hamiltonian and the other ones on all terms save H . With this result one then finds an expression for (51). If this expression is used in (50) we get the energy balance equation

$$\frac{\partial}{\partial t} (\frac{1}{2} q \mathbf{v}^2 + q u^K) = - \nabla \cdot \{ \mathbf{v} (\frac{1}{2} q \mathbf{v}^2 + q u^K) + \mathbf{P}^K \cdot \mathbf{v} + \mathbf{J}_q^K \} + \Psi^L + \Psi^S. \quad (53)$$

The energy density $q u^K$ is found as:

$$q u^K = \int \left\{ \frac{1}{2} m \hat{\mathbf{v}}_1^2 + \frac{1}{2} \sum_i m_i (\partial_{tP} \mathbf{r}_{1i})^2 + \sum_{i,j(i \neq j)} \frac{e_i e_j}{8\pi |\mathbf{r}_{1i} - \mathbf{r}_{1j}|} \right\} f_1(\mathbf{R}, 1; t) d1 \quad (54)$$

with the masses and charges $m_{ki} = m_i$ and $e_{ki} = e_i$ of the constituent par-

ticles of the identical atoms and the velocity fluctuation \hat{v}_1 defined by (42). Furthermore the kinetic pressure \mathbf{P}^K has been given in (44) and the macroscopic power densities Ψ^L and Ψ^S stand for

$$\Psi^{L,S} \equiv \int \sum_k \psi_k^{L,S} \delta(\mathbf{R}_k - \mathbf{R}) \rho(1, \dots, N; t) d1 \dots dN \quad (55)$$

with atomic quantities given in (VI.106) and (VI.107). All quantities mentioned so far have the same form as those occurring in the classical theory with the distribution function replaced by a Wigner function. The heat flow \mathbf{J}_q^K , however, has a form which differs from the corresponding classical expression (II.81):

$$\begin{aligned} \mathbf{J}_q^K = \int \hat{v}_1 \left\{ \frac{1}{2} m \hat{v}_1^2 + \frac{1}{2} \sum_i m_i (\partial_{iP} \mathbf{r}_{1i})^2 + \sum_{i,j(i \neq j)} \frac{e_i e_j}{8\pi |\mathbf{r}_{1i} - \mathbf{r}_{1j}|} \right\} f_1(\mathbf{R}, 1; t) d1 \\ + \int \sum_i \frac{\hbar^2}{8} \frac{e_i}{m m_i c} \Delta_{1i} A_e(\mathbf{R}_{1i}, t) f_1(\mathbf{R}, 1; t) d1. \quad (56) \end{aligned}$$

The last term with the Laplacian of the vector potential A_e has arisen from the second term of the expression (52). The occurrence of this rather exotic term does not destroy gauge invariance, as may be seen by writing down the operator of which (56) is the average (see problem 1):

$$\begin{aligned} \sum_k \sum_{i,j} \frac{1}{16m_k m_{ki}} \{ \mathbf{P}_{kj,op} - c^{-1} e_{kj} A_e(\mathbf{R}_{kj,op}, t) - m_{kj} \mathbf{v}(\mathbf{R}, t), \\ \{ (\mathbf{P}_{ki,op} - c^{-1} e_{ki} A_e(\mathbf{R}_{ki,op}, t) - m_{ki} \mathbf{v}(\mathbf{R}, t)), \\ \{ (\mathbf{P}_{ki,op} - c^{-1} e_{ki} A_e(\mathbf{R}_{ki,op}, t) - m_{ki} \mathbf{v}(\mathbf{R}, t)), \delta(\mathbf{R}_{k,op} - \mathbf{R}) \} \} \} \\ + \sum_k \sum_i \frac{1}{2m_k} \left\{ \mathbf{P}_{ki,op} - c^{-1} e_{ki} A_e(\mathbf{R}_{ki,op}, t) - m_{ki} \mathbf{v}(\mathbf{R}, t), \right. \\ \left. \sum_{p,s(p \neq s)} \frac{e_{kp} e_{ks}}{8\pi |\mathbf{r}_{kp,op} - \mathbf{r}_{ks,op}|} \delta(\mathbf{R}_{k,op} - \mathbf{R}) \right\}, \quad (57) \end{aligned}$$

where the curly brackets indicate anticommutators. The fact that the vector potential appears in the traditional combination with the momentum operator guarantees the gauge invariance¹.

¹ As is well known the canonical commutation relations for coordinate and momentum operators are invariant under the von Neumann transformation $\mathbf{P}_{op} \rightarrow \mathbf{P}'_{op} \equiv \mathbf{P}_{op} + \nabla \chi$ with χ an arbitrary function of the coordinate operators. As a consequence the combination $\mathbf{P}_{op} - c^{-1} e A_{op}$ may be written as $\mathbf{P}'_{op} - \nabla \chi - c^{-1} e A_{op}$. Since under a gauge transformation the vector potential A_{op} becomes $A'_{op} = A_{op} + \nabla \psi$ (with arbitrary ψ), it follows that $\mathbf{P}_{op} - c^{-1} e A_{op}$ can be written as $\mathbf{P}'_{op} - c^{-1} e A'_{op}$, if χ is chosen as $c^{-1} e \psi$.

The energy balance equation (53) contains the long range and short range power densities (55), which may be evaluated along the same lines as in the classical treatment (section 5d of chapter II). The point which has to be checked in detail is the validity of the quantum-mechanical analogue of (II.83). This may be done in the same way as in (46-47). As a result one finds for the long range power density (55) (cf. (II.88))

$$\psi^L = \mathbf{J} \cdot \mathbf{E} + \frac{\partial \mathbf{P}}{\partial t} \cdot \mathbf{E} + \nabla \cdot (\mathbf{v} \mathbf{P} \cdot \mathbf{E}) - \mathbf{M} \cdot \frac{\partial \mathbf{B}}{\partial t} - \nabla \cdot (\mathbf{P}^F \cdot \mathbf{v} + \mathbf{J}_q^F) + \Psi^C, \quad (58)$$

where all quantities have the same form as in classical theory with the distribution functions replaced by Wigner functions and also fluxion dots by the operation ∂_{iP} . The same applies to the short range power density Ψ^S .

e. The short range terms

Since the integrand in \mathbf{F}^S , which is of the form (II.75), vanishes with increasing $|s|$, one may expand the Wigner function in powers of s as the distribution function in the classical treatment. Then one finds that

$$\mathbf{F}^S = -\nabla \cdot \mathbf{P}^S \quad (59)$$

with a pressure contribution \mathbf{P}^S of the same form as (II.94).

As to the short range power density Ψ^S , an expansion of the two-point Wigner function leads to a relation of the form (II.95). It may be written in an alternative way by considering the derivative of a quantity of the form (II.97) namely

$$\begin{aligned} qu^S = \int \sum_{k,l(k \neq l)} \left(\sum_{i,j} \frac{e_{ki} e_{lj}}{8\pi |s + \mathbf{r}_{ki} - \mathbf{r}_{lj}|} - \sum_{n,m=0}^{\infty} (-1)^n \overline{\mu}_k^{(n)} : \nabla_s \overline{\mu}_l^{(m)} : \nabla_s^m \frac{1}{8\pi s} \right) \\ \delta(\mathbf{R}_k - \mathbf{R} - \frac{1}{2}s) \delta(\mathbf{R}_l - \mathbf{R} + \frac{1}{2}s) \rho(1, \dots, N; t) d1 \dots dN, \quad (60) \end{aligned}$$

which contains the N -point Wigner function. Its time derivative follows by application of (13) with the Weyl transform (VI.61) of the Hamiltonian. One obtains an equation of the same form as (II.99) with distribution functions replaced by Wigner functions and fluxion dots by the symbol ∂_{iP} . As a consequence the short range power density becomes (cf. (II.101)):

$$\Psi^S = -\nabla \cdot (\mathbf{v} qu^S + \mathbf{P}^S \cdot \mathbf{v} + \mathbf{J}_q^S) - \frac{\partial qu^S}{\partial t} \quad (61)$$

with qu^S given by (60) and \mathbf{J}_q^S by an expression of the same form as (II.96, 100).

f. *The correlation contributions*

The correlation contributions F^C and Ψ^C will be studied here for a fluid system of neutral atoms. (The other cases, namely plasmas and systems with long range correlations, that have been studied in the classical treatment, may be generalized to quantum theory in an analogous fashion.)

In classical theory fluid systems of neutral atoms were characterized by the existence of a correlation length that is small compared to the distance over which the macroscopic quantities change appreciably. Therefore the correlation function could be expanded in a Taylor series, which could be broken off after a few terms (the Irving–Kirkwood approximation). In quantum mechanics two reasons for the occurrence of correlations exist: in the first place correlation effects that are the quantum-mechanical analogues of the classical correlation effects due to the interaction between the particles, and furthermore the correlation effects due to statistics, which take place even in a perfect gas. The latter effects are characterized by a ‘correlation length’ which is of the order of the thermal wave length $\lambda \equiv h/(2\pi mkT)^{\frac{1}{2}}$ as is shown in the appendix I. A necessary condition for the expansion of the correlation Wigner function is hence that the thermal wave length λ is small compared to the distance d over which the macroscopic quantities change appreciably, i.e. for sufficiently high temperature. (This does not mean that quantum effects due to statistics are now neglected altogether. That would require the smallness of the thermal wave length λ with respect to the mean free path; the latter is always much smaller than the distance d in the physical situations to which statistical mechanics applies.) The second condition for the possibility of expanding the correlation Wigner function is the smallness of the correlation length due to the atomic interactions with respect to the macroscopic distance d . The latter condition sets a limit to the applicability of the Irving–Kirkwood procedure of the same kind as in the classical case.

If indeed the system is such that the Wigner correlation function has short range in the sense described above, we may apply the Irving–Kirkwood approximation to the correlation force density F^C and the correlation power density Ψ^C . Then one may write

$$F^C = -\nabla \cdot \mathbf{P}^C, \quad (62)$$

$$\Psi^C = -\nabla \cdot (\mathbf{v}qu^C + \mathbf{P}^C \cdot \mathbf{v} + \mathbf{J}_q^C) - \frac{\partial qu^C}{\partial t}, \quad (63)$$

with \mathbf{P}^C , \mathbf{J}_q^C and qu^C given by formulae of the same form as (II.104), (II.111) and (II.112), but with a Wigner function instead of a classical distribution function and the Poisson bracket derivative ∂_{iP} instead of the fluxion dot.

(In taking the time derivative of the quantity qu^C , one has to apply the identity (13); owing to the special form of the integrand of qu^C and the Weyl transform of the Hamiltonian, the sine operator reduces to the Poisson bracket operator.)

If the Wigner correlation function has long range character one may use an artifice of the same type as in chapter II, section 5*h* of the classical theory to derive again expressions of the form (62–63), but with a mean Wigner correlation function instead of the Wigner correlation function itself.

g. *Substances with short range correlations*

Collecting the results of the preceding subsections we have found the momentum law for substances of neutral atoms of which the Wigner correlation functions have short range:

$$\frac{\partial qv}{\partial t} = -\nabla \cdot (qv\mathbf{v} + \mathbf{P}) + (\nabla E) \cdot \mathbf{P} + (\nabla \mathbf{B}) \cdot \mathbf{M} + c^{-1} \frac{\partial}{\partial t} (\mathbf{P} \wedge \mathbf{B}) + c^{-1} \nabla \cdot (\mathbf{v} \mathbf{P} \wedge \mathbf{B}) \quad (64)$$

(cf. (II.105–106)). Hence the time derivative of the momentum density qv is equal to the sum of a divergence of a material term, that contains the pressure tensor \mathbf{P} , and a force density due to the electromagnetic field.

The energy law for such substances is

$$\begin{aligned} \frac{\partial}{\partial t} (\frac{1}{2}qv^2 + qu) = & -\nabla \cdot \{v(\frac{1}{2}qv^2 + qu) + \mathbf{P} \cdot \mathbf{v} + \mathbf{J}_q\} \\ & + \frac{\partial \mathbf{P}}{\partial t} \cdot \mathbf{E} + \nabla \cdot (\mathbf{v} \mathbf{P} \cdot \mathbf{E}) - \mathbf{M} \cdot \frac{\partial \mathbf{B}}{\partial t}. \end{aligned} \quad (65)$$

(cf. (II.113–114)). The change of the total energy density with time is thus due to a material energy flow and a power density, which arises from the electromagnetic fields. The difference with the classical results consists in the replacement of the classical distribution functions by Wigner functions and fluxion dots by the operator ∂_{iP} in the expressions for the macroscopic quantities. Moreover an extra term with the Laplacian of the external vector potential appears in the contribution \mathbf{J}_q^K to the heat flow.

Just as in classical theory the balance equations (64) and (65) may be written in the form of conservation laws. One then obtains equations of the form (II.109) and (II.118).

The quantum-mechanical non-relativistic treatment of neutral plasma’s and of substances with long range Wigner correlations presents no new aspects as compared to the classical non-relativistic theory.

Galilei invariance of the theory, i.e. invariance with respect to the coordinate transformation

$$\mathbf{R}' = \mathbf{R} + \mathbf{V}t, \quad t' = t, \quad (66)$$

follows from the transformation of the wave function¹

$$\psi'(\mathbf{R}', t') = \exp \left\{ \frac{i}{\hbar} \left(\sum_{k,i} \mathbf{V} \cdot \mathbf{R}_{ki} + \frac{1}{2} \sum_{ki} m_{ki} V^2 t \right) \right\} \psi(\mathbf{R}, t). \quad (67)$$

In fact the Hamilton operator that governs the time behaviour of the wave function transforms as

$$H'_{\text{op}}(\mathbf{P}_{ki,\text{op}}, \mathbf{R}_{ki,\text{op}}) = H_{\text{op}}(\mathbf{P}_{ki,\text{op}}, \mathbf{R}_{ki,\text{op}} - \mathbf{V}t) + c^{-1} \sum_{ki} e_{ki} \mathbf{V} \cdot \mathbf{A}_c(\mathbf{R}_{ki,\text{op}} - \mathbf{V}t, t). \quad (68)$$

The Weyl transform of this Hamiltonian occurs in the Poisson bracket $\partial_{t'p}$. The transformation of the Wigner function that follows from its definition (4–5) and (67) is

$$\rho'(\mathbf{P}_{ki}, \mathbf{R}_{ki}; t) = \rho(\mathbf{P}_{ki} - m_{ki} \mathbf{V}, \mathbf{R}_{ki} - \mathbf{V}t; t). \quad (69)$$

With (68) and (69) one may check the Galilei invariance of the equations.

6 The angular momentum equations

If one starts from the atomic angular momentum equation (VI.111) with (VI.112) and (VI.113) one finds the macroscopic angular momentum equation by multiplying with the delta function $\delta(\mathbf{R}_k - \mathbf{R})$, summing over k , multiplying with a Wigner function and integrating over phase space. Since the Weyl transform of the atomic inner angular momentum density $\sum_k \bar{s}_k \delta(\mathbf{R}_k - \mathbf{R})$ is linear in the momenta, the sine occurring in the time derivative (13) reduces to the Poisson bracket. Therefore the angular momentum law has the same form as in classical theory, if one supposes again the Irving–Kirkwood approximation applicable. The result is then for a substance of neutral atoms with short range Wigner correlation functions:

$$\frac{\partial \mathbf{S}}{\partial t} = -\mathbf{V} \cdot (\mathbf{v} \mathbf{S} + \mathbf{J}_s) + \mathbf{D}_s + \mathbf{P} \wedge \mathbf{E} + \mathbf{M} \wedge \mathbf{B} + c^{-1} \mathbf{v} \wedge (\mathbf{P} \wedge \mathbf{B}). \quad (70)$$

This law has the same form as (II.185), but in the statistical expressions Wigner functions occur instead of classical distribution functions. It con-

¹ J. M. Lévy-Leblond, J. Math. Phys. 4(1963)776; see also problem 2.

tains the inner angular momentum density \mathbf{S} , the (conduction part of the) inner angular momentum flow \mathbf{J}_s , (which has the form (II.186)), the material part of the source term \mathbf{D}_s (of the form (II.187)) and torque densities exerted by the electromagnetic fields (\mathbf{E}, \mathbf{B}) on the polarization densities (\mathbf{P}, \mathbf{M}) .

The macroscopic quantities have been written throughout as integrals over Weyl transforms of atomic operators and Wigner functions. Therefore they are averages of operators that may be found from these Weyl transforms. In particular one finds that the macroscopic inner angular momentum density is the average of the atomic operator

$$\frac{1}{2} \sum_k \{ \bar{s}_{k,\text{op}}, \delta(\mathbf{R}_{k,\text{op}} - \mathbf{R}) \}. \quad (71)$$

The inner angular momentum operator $\bar{s}_{k,\text{op}}$ has the Weyl transform (VI.110) and is hence:

$$\bar{s}_{k,\text{op}} = \frac{1}{2} \sum_i m_{ki} \{ \mathbf{r}_{ki,\text{op}} \wedge, \dot{\mathbf{r}}_{ki,\text{op}} \}, \quad (72)$$

where $\mathbf{r}_{ki,\text{op}}$ stands for $\mathbf{R}_{ki,\text{op}} - \mathbf{R}_{k,\text{op}}$ and where $\dot{\mathbf{r}}_{ki,\text{op}}$ is given by (VI.95).

In the same way as in classical theory one may prove that the source term \mathbf{D}_s is equal to minus the antisymmetric part of the pressure tensor

$$\mathbf{D}_s = -\mathbf{P}_A \quad (73)$$

(cf. (II.195)). This fact has as a consequence that also the conservation law of total angular momentum in the form (II.197) is valid here.

7 The laws of thermodynamics

a. The first law

The first law of thermodynamics is a direct consequence of the energy balance equation. Since the latter has the same form as in the classical treatment, one finds in the case of a system of neutral atoms with short range Wigner correlations an equation as (II.213), i.e.

$$\frac{dq}{dt} = \frac{du}{dt} + v \bar{\mathbf{P}} : \nabla \mathbf{v} - \frac{d(v \mathbf{P}')}{dt} \cdot \mathbf{E}' + v \mathbf{M}' \cdot \frac{d\mathbf{B}'}{dt}. \quad (74)$$

It shows that the heat supplied per unit mass and time is equal to the change of specific internal energy u plus a viscous term with the pressure tensor \mathbf{P} and the velocity gradients, plus two terms with the electromagnetic fields \mathbf{E}' , \mathbf{B}' and the polarization densities \mathbf{P}' , \mathbf{M}' (II.188) in the rest frame. The time derivatives at the right-hand side are material time derivatives $(\partial/\partial t + \mathbf{v} \cdot \nabla)$, and v is the specific volume.

For neutral plasmas and for systems with long range correlations one finds laws of the form (II.216) and (II.217).

b. *The second law*

In order to derive the second law for a fluid system of neutral atoms we consider a large polarized system at rest, divided into nearly uniform cells and describe these cells by canonical ensembles with the environments playing the role of heat baths. The cells are chosen to be ellipsoidal, so that the external fields due to the surroundings of the cells are uniform and given by (II.220) with (II.219).

The quantum-mechanical canonical ensemble is given by a density operator

$$P_{op} = \exp \{ (F^* - H_{op}^W) / kT \}, \tag{75}$$

so that, since $\text{Tr } P_{op} = 1$, one has

$$\exp (-F^* / kT) = \text{Tr} \exp (-H_{op}^W / kT). \tag{76}$$

Here F^* is the free energy, T the temperature and H_{op}^W is the Hamilton operator of the system with the inclusion of wall potential operators

$$H_{op}^W = H_{op} + \sum_k U_{k,op}^W(\mathbf{R}_{k,op}). \tag{77}$$

The wall potential operator $U_{k,op}^W$, which depends on the centre of mass operator $\mathbf{R}_{k,op}$ of atom k , is defined in such a way that it gives infinity if it operates on an eigenfunction of $\mathbf{R}_{k,op}$ with eigenvalue \mathbf{R}_k lying outside the volume V , while it gives zero if it operates on an eigenfunction of $\mathbf{R}_{k,op}$ with eigenvalue \mathbf{R}_k lying inside the volume V . The Hamilton operator H_{op} may be written as a function of the coordinate and momentum operators of all constituent particles of the system, or alternatively as a function of the centre of mass and relative coordinate operators and corresponding momentum operators. The latter form of the Hamilton operator has been derived in appendix II. Its Weyl transform is (A54) with $e_k = 0$:

$$\begin{aligned} H_{op}(\mathbf{p}_{op}, \mathbf{q}_{op}, t) \rightleftharpoons & \sum_k \left(\frac{\mathbf{P}_k^2}{2m_k} + \sum_{i=1}^{f-1} \frac{\mathbf{P}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{\mathbf{P}_{ki} \cdot \mathbf{P}_{kj}}{2m_k} \right) \\ & + \sum_k \sum_{i,j=1(i \neq j)}^f \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki} - \mathbf{R}_{kj}|} + \sum_{k,l(k \neq l)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki} - \mathbf{R}_{lj}|} \\ & - \sum_k \left\{ \bar{\mu}_k^{(1)} \cdot \left(\mathbf{E}_c + \frac{1}{2} c^{-1} \frac{\mathbf{P}_k}{m_k} \wedge \mathbf{B}_c \right) + \frac{1}{2} c^{-1} (\partial_{iP} \bar{\mu}_k^{(1)}) \cdot (\mathbf{B}_c \wedge \mathbf{R}_k) + \bar{v}_k^{(1)} \cdot \mathbf{B}_c \right\} \tag{78} \end{aligned}$$

with the Weyl transforms of the electric and magnetic dipole moments:

$$\bar{\mu}_k^{(1)}(\mathbf{q}) = \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{q}_{kf} \}, \tag{79}$$

$$\bar{v}_k^{(1)}(\mathbf{p}, \mathbf{q}) = \frac{1}{2} c^{-1} \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{q}_{kf} \} \wedge \left\{ (1 - \delta_{if}) \frac{\mathbf{p}_{ki}}{m_{ki}} - \sum_{j=1}^{f-1} \frac{\mathbf{p}_{kj}}{m_k} \right\}.$$

The Hamilton operator (78) depends on the external electric and magnetic fields $(\mathbf{E}_c, \mathbf{B}_c)$, and the wall potential operators on the boundary of the system. Hence the free energy depends on these quantities and on the temperature T . The partial derivative of the free energy with respect to the external electric field is:

$$\frac{\partial F^*}{\partial \mathbf{E}_c} = -kT e^{F^*/kT} \text{Tr} \left\{ \frac{\partial}{\partial \mathbf{E}_c} \exp (-H_{op}^W / kT) \right\}. \tag{80}$$

We now apply an identity¹ for the derivative of an exponential operator:

$$\frac{\partial}{\partial \alpha} e^{A_{op}(\alpha)} = \sum_{n=0}^{\infty} \frac{1}{(n+1)!} A_{op}^{(n)}(\alpha) e^{A_{op}(\alpha)} \tag{81}$$

with the operator $A_{op}^{(n)}(\alpha)$ following from

$$A_{op}^{(0)} \equiv \frac{\partial A_{op}(\alpha)}{\partial \alpha}, \quad A_{op}^{(n)} = [A_{op}, A_{op}^{(n-1)}] \tag{82}$$

(cf. problem 3). Using this lemma in (80) one finds, since the traces of the commutators occurring vanish,

$$\frac{\partial F^*}{\partial \mathbf{E}_c} = \text{Tr} \left[\frac{\partial H_{op}}{\partial \mathbf{E}_c} \exp \{ (F^* - H_{op}^W) / kT \} \right], \tag{83}$$

where the fact that the wall potential operator is independent of the fields has been taken into account. This expression may be written in terms of Wigner functions and the Weyl transform of $\partial H_{op} / \partial \mathbf{E}_c$. The latter is equal to $\partial H / \partial \mathbf{E}_c$:

$$\frac{\partial H_{op}}{\partial \mathbf{E}_c} \rightleftharpoons \frac{\partial H}{\partial \mathbf{E}_c} = - \sum_k \bar{\mu}_k^{(1)}. \tag{84}$$

Thus one finds for (83)

$$\frac{\partial F^*}{\partial \mathbf{E}_c} = - \int \bar{\mu}_1^{(1)} f_1(1) d1 = -VP, \tag{85}$$

¹ R. J. Riddell jr. and G. E. Uhlenbeck, J. Chem. Phys. 18(1950)1066.

where we employed the reduced Wigner function $f_1(1)$ and took the uniformity of the electric polarization density \mathbf{P} (formula (28) for the dipole case) into account. Likewise we find for the derivative with respect to the magnetic field

$$\frac{\partial F^*}{\partial \mathbf{B}_e} = \text{Tr} \left[\frac{\partial H_{\text{op}}}{\partial \mathbf{B}_e} \exp \left\{ (F^* - H_{\text{op}}^W) / kT \right\} \right]. \quad (86)$$

With the help of the Weyl correspondence

$$\frac{\partial H_{\text{op}}}{\partial \mathbf{B}_e} \rightleftharpoons \frac{\partial H}{\partial \mathbf{B}_e} = - \sum_k \left\{ \bar{\mathbf{v}}_k^{(1)} + \frac{1}{2} c^{-1} \bar{\boldsymbol{\mu}}_k^{(1)} \wedge \frac{\mathbf{P}_k}{m_k} - \frac{1}{2} c^{-1} (\partial_{i\mathbf{P}} \bar{\boldsymbol{\mu}}_k^{(1)}) \wedge \mathbf{R}_k \right\} \quad (87)$$

(with $\partial_{i\mathbf{P}}$ given by (VI.72)) that follows from (78), one obtains then

$$\frac{\partial F^*}{\partial \mathbf{B}_e} = - \int \left\{ \bar{\mathbf{v}}_1^{(1)} + \frac{1}{2} c^{-1} \bar{\boldsymbol{\mu}}_1^{(1)} \wedge \frac{\mathbf{P}_1}{m_1} - \frac{1}{2} c^{-1} (\partial_{i\mathbf{P}} \bar{\boldsymbol{\mu}}_1^{(1)}) \wedge \mathbf{R}_1 \right\} f_1(1) d1. \quad (88)$$

Since the canonical ensemble is stationary one derives by application of (13) that, up to order c^0 ,

$$\int (\partial_{i\mathbf{P}} \bar{\boldsymbol{\mu}}_1^{(1)}) \wedge \mathbf{R}_1 f_1(1) d1 = - \int \bar{\boldsymbol{\mu}}_1^{(1)} \wedge \frac{\mathbf{P}_1}{m_1} f_1(1) d1, \quad (89)$$

where $\mathbf{P}_1/m_1 = \partial_{i\mathbf{P}} \mathbf{R}_1 \equiv \mathbf{v}_1$ (up to order c^0). Therefore (88) may be written as

$$\frac{\partial F^*}{\partial \mathbf{B}_e} = - \int \left(\bar{\mathbf{v}}_1^{(1)} + c^{-1} \bar{\boldsymbol{\mu}}_1^{(1)} \wedge \frac{\mathbf{P}_1}{m_1} \right) f_1(1) d1 = -VM, \quad (90)$$

because of the definition (28) of the (uniform) magnetic polarization density \mathbf{M} for the dipole case.

By definition the partial derivative of the free energy with respect to the temperature is equal to minus the entropy:

$$\frac{\partial F^*}{\partial T} = -S. \quad (91)$$

Just as in the classical case infinitesimal changes of the boundary will be described by a uniform deformation tensor $\delta \boldsymbol{\epsilon}$ in such a way that

$$\delta \mathbf{R} = \delta \boldsymbol{\epsilon} \cdot \mathbf{R}, \quad (92)$$

with the centre of the system as the origin of coordinates.

The total change of the free energy follows from (85), (90) and (91) as

$$\delta F^* = -S \delta T - V \mathbf{P} \cdot \delta \mathbf{E}_e - V \mathbf{M} \cdot \delta \mathbf{B}_e + \mathbf{A} : \delta \boldsymbol{\epsilon} \quad (93)$$

with an as yet unspecified tensor \mathbf{A} .

The free energy is the difference of the canonical average of the Hamilton operator and the product of the temperature and the entropy. To find an expression for the average of the Hamilton operator, we shall employ its Weyl transform in the form (A57) with atomic charges $e_k = 0$:

$$H_{\text{op}}(\mathbf{p}_{\text{op}}, \mathbf{q}_{\text{op}}) \rightleftharpoons K + \sum_k \sum_{i,j=1(i \neq j)}^f \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki} - \mathbf{R}_{kj}|} + \sum_{k,l(k \neq l)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki} - \mathbf{R}_{lj}|} - \sum_k \bar{\boldsymbol{\mu}}_k^{(1)} \cdot \mathbf{E}_e, \quad (94)$$

with the quantity K defined as

$$K = \sum_{k,i} \frac{1}{2} m_{ki} (\partial_{i\mathbf{P}} \mathbf{R}_{ki})^2. \quad (95)$$

The canonical average of the Hamilton operator follows by multiplication of the right-hand side of (94) with the Wigner function that belongs to the canonical ensemble and integration over phase space. Then one arrives at an expression which has the same form as that of the classical treatment. Along the same lines of reasoning as followed there one finds¹ for systems with a short range Wigner correlation function as the average Hamilton operator

$$V(q_u + \frac{1}{2} \mathbf{P} \mathbf{P} : \mathbf{L} - \mathbf{P} \cdot \mathbf{E}_e), \quad (96)$$

where \mathbf{L} is the depolarizing tensor and u the specific internal energy.

The tensor \mathbf{A} , which occurs in (93), is equal to

$$\mathbf{A} = - \int \sum_k \left(\frac{\partial H}{\partial \mathbf{P}_k} \mathbf{P}_k - \mathbf{R}_k \frac{\partial H}{\partial \mathbf{R}_k} \right) \rho(1, \dots, N) d1 \dots dN, \quad (97)$$

as shown in the appendix III. With the form (78) of the Weyl transform of the Hamilton operator one finds for \mathbf{A} :

$$\mathbf{A} = - \int \sum_k \left[m_k \mathbf{v}_k \left(\mathbf{v}_k - \frac{1}{2} c^{-1} \frac{\bar{\boldsymbol{\mu}}_k^{(1)}}{m_k} \wedge \mathbf{B}_e \right) - \mathbf{R}_k \left\{ \bar{\mathbf{v}}_k \sum_{i(\neq k)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki} - \mathbf{R}_{lj}|} - \frac{1}{2} c^{-1} (\partial_{i\mathbf{P}} \bar{\boldsymbol{\mu}}_k^{(1)}) \wedge \mathbf{B}_e \right\} \right] \rho(1, \dots, N) d1 \dots dN, \quad (98)$$

¹ The vanishing of the wave function outside the system leads to the vanishing of the Wigner function there, owing to the convexity of the ellipsoid (see the definition (5)).

with $\mathbf{v}_k \equiv \partial_{i\mathbf{p}} \mathbf{R}_k$. From the stationary character of the canonical ensemble together with formula (13) it follows that

$$\int \sum_k \{ \mathbf{v}_k \bar{\mu}_k^{(1)} \wedge \mathbf{B}_c + \mathbf{R}_k (\partial_{i\mathbf{p}} \bar{\mu}_k^{(1)}) \wedge \mathbf{B}_c \} \rho(1, \dots, N) d1 \dots dN = 0, \quad (99)$$

so that the expression (98) now becomes:

$$\mathbf{A} = - \int \sum_k \left\{ m_k \mathbf{v}_k \left(\mathbf{v}_k - c^{-1} \frac{\bar{\mu}_k^{(1)}}{m_k} \wedge \mathbf{B}_c \right) - \mathbf{R}_k \nabla_k \sum_{l(\neq k)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki} - \mathbf{R}_{lj}|} \right\} \rho(1, \dots, N) d1 \dots dN. \quad (100)$$

This expression is again of the same form as that of classical theory (with the classical distribution function replaced by the Wigner function and the fluxion dot by the operator $\partial_{i\mathbf{p}}$). Therefore we obtain, as in classical theory, for a system with short range Wigner correlations:

$$\mathbf{A} = -V(\mathbf{P} + \frac{1}{2}\mathbf{K} : \mathbf{P}\mathbf{P}), \quad (101)$$

with \mathbf{P} the pressure tensor, \mathbf{K} the tensor (II.236), \mathbf{P} the electric polarization and V the volume. Collecting the results (93), (96) and (101), and eliminating the external fields ($\mathbf{E}_c, \mathbf{B}_c$) in favour of the Maxwell fields (\mathbf{E}, \mathbf{B}) (II.220), we get for the entropy change per unit of mass:

$$T\delta s = \delta u + v\mathbf{P} : \delta\epsilon - \mathbf{E} \cdot \delta(v\mathbf{P}) + v\mathbf{M} \cdot \delta\mathbf{B}, \quad (102)$$

where s is the specific entropy and v the specific volume.

For fluids (isotropic in the absence of polarizations and fields) in which the polarization densities depend on the specific volume, the temperature and the Maxwell fields, one finds by the same reasoning as in the classical theory that the non-relativistic second law (or Gibbs relation) is

$$Tds = du + p dv - \mathbf{E} \cdot d(v\mathbf{P}) + v\mathbf{M} \cdot d\mathbf{B}. \quad (103)$$

The quantities occurring here are all defined for a system at rest. This formula shows that for such fluids at equilibrium the pressure tensor \mathbf{P} is a multiple p of the unit tensor.

From the combination of the first and second law (for local equilibrium) one may derive the entropy balance equation, just as in classical theory.

The second laws for amorphous or polycrystalline substances, for neutral plasmas and for systems with long range Wigner correlation functions have the same form as the corresponding classical laws, as may be shown by a reasoning analogous to that given above for a fluid with short range Wigner correlations.

The Wigner function in statistical mechanics

a. Definition

In statistical mechanics one does not consider pure states of N -particle systems, but an ensemble of pure states, i.e. a mixed state, described by a density operator¹

$$P(t) = \sum_{\gamma} w_{\gamma} |\psi_{\gamma}(t)\rangle \langle \psi_{\gamma}(t)|, \quad (A1)$$

where the $|\psi_{\gamma}(t)\rangle$ form a complete orthonormal set and the w_{γ} are statistical weights normalized to unity

$$\sum_{\gamma} w_{\gamma} = 1. \quad (A2)$$

Then the Wigner function, which is the Weyl transform of the density operator (times \hbar^3) becomes a weighted sum of Wigner functions of pure states

$$\rho(\mathbf{p}, \mathbf{q}; t) = \sum_{\gamma} w_{\gamma} \rho_{\gamma}(\mathbf{p}, \mathbf{q}; t), \quad (A3)$$

where the partial Wigner function ρ_{γ} is, according to (VI.A65)

$$\rho_{\gamma}(\mathbf{p}, \mathbf{q}; t) = \hbar^{-3} \int d\mathbf{v} e^{(i/\hbar)\mathbf{p}\cdot\mathbf{v}} \psi_{\gamma}(\mathbf{q} - \frac{1}{2}\mathbf{v}; t) \psi_{\gamma}^*(\mathbf{q} + \frac{1}{2}\mathbf{v}; t). \quad (A4)$$

Alternatively one may use here (VI.A66–68).

The average value

$$\bar{A}(t) = \text{Tr} \{ P(t)A \} \quad (A5)$$

of a quantity, which is given by an operator A , may be written with the help of the Wigner function (A3) as:

$$\bar{A}(t) = \bar{a}(t) \equiv \int d\mathbf{p} d\mathbf{q} \rho(\mathbf{p}, \mathbf{q}; t) a(\mathbf{p}, \mathbf{q}), \quad (A6)$$

just as in (VI.A62–63), with $a(\mathbf{p}, \mathbf{q})$ the Weyl transform of the operator A . (For an N -particle system the integration is $6N$ -fold.) From (A2) and the

¹ In this appendix we use capitals for operators and lower case symbols for c -numbers.

normalization (VI.A69) of the partial Wigner functions $\rho_\gamma(\mathbf{p}, \mathbf{q}; t)$ it follows that the total Wigner function is normalized

$$\int d\mathbf{p} d\mathbf{q} \rho(\mathbf{p}, \mathbf{q}; t) = 1. \quad (\text{A7})$$

b. Properties

The Wigner function can not be interpreted as a probability density, since it is not necessarily positive definite, although it is real and normalized and permits to calculate average values according to (A6). The integrals over the coordinates or momenta however may be interpreted as probability densities, since they are positive definite:

$$\int d\mathbf{p} \rho(\mathbf{p}, \mathbf{q}; t) = \sum_\gamma w_\gamma |\psi_\gamma(\mathbf{q}; t)|^2 \geq 0, \quad (\text{A8})$$

$$\int d\mathbf{q} \rho(\mathbf{p}, \mathbf{q}; t) = \sum_\gamma w_\gamma |\varphi_\gamma(\mathbf{p}; t)|^2 \geq 0, \quad (\text{A9})$$

as follows from (A3) and (A4) and the analogous formula with the wave function in the momentum representation.

The partial Wigner functions $\rho_\gamma(\mathbf{p}, \mathbf{q}; t)$ for pure states fulfil an inequality of the form (VI.A72). Since the total Wigner function is the weighted sum of pure state Wigner functions, it fulfils the same inequality

$$|\rho(\mathbf{p}, \mathbf{q}; t)| \leq (2/h)^3. \quad (\text{A10})$$

For mixed states the density operator is not idempotent, since now

$$P^2(t) = \sum_\gamma w_\gamma^2 |\psi_\gamma(t)\rangle \langle \psi_\gamma(t)|, \quad (\text{A11})$$

as follows from (A1) and the orthonormality of $|\psi_\gamma(t)\rangle$. Clearly this is only equal to $P(t)$ (A1) if w_γ is 0 or 1 and hence according to (A2) if only one single w_γ is 1 and the rest zero (a pure state). It follows from (A11) and (A1-2) with the orthogonality of the state vectors $|\psi_\gamma(t)\rangle$ and the inequality $\sum_\gamma w_\gamma^2 \leq \sum_\gamma w_\gamma$ that

$$\text{Tr} \{P(t)^2\} \leq 1. \quad (\text{A12})$$

Here the equality sign refers to the pure state. From (A12), (VI.A53) and the fact that the Wigner function is the Weyl transform of the density operator one finds that

$$\int d\mathbf{p} d\mathbf{q} \{\rho(\mathbf{p}, \mathbf{q}; t)\}^2 \leq h^{-3}. \quad (\text{A13})$$

Again the equality sign holds for the pure state (cf. (VI.A75)).

The development in time of the Wigner function for a mixed state is governed by the same laws as those for a pure state (v. (VI.A89)).

c. Reduced Wigner functions

For the description of systems containing N identical particles it is useful to introduce reduced Wigner functions. These functions are obtained from the Wigner function $\rho(1, 2, \dots, N; t)$, which depends on all momentum and coordinate variables of the particles, by integrating over the momentum and coordinate variables of a number of particles. They are convenient if one considers the averages of physical quantities which are sum functions. For instance if a physical quantity has the operator form

$$A = \sum_{i=1}^N A_i, \quad (\text{A14})$$

where A_i depends on the coordinate and momentum operators of particle i , its Weyl transform is

$$A \rightleftharpoons a(1, \dots, N) = \sum_{i=1}^N a_i(i) \quad (\text{A15})$$

and its average is according to (A6)

$$\bar{A}(t) = N \int a_1(1) \rho(1, 2, \dots, N; t) d1 \dots dN. \quad (\text{A16})$$

This may be written as

$$\bar{A}(t) = \int a_1(1) f_1(1; t) d1 \quad (\text{A17})$$

with the one-point reduced Wigner function defined as

$$f_1(1; t) = N \int \rho(1, 2, \dots, N; t) d2 \dots dN, \quad (\text{A18})$$

normalized to N .

Likewise if a physical quantity is a two-point function, i.e. if

$$A = \sum_{i,j=1(i \neq j)}^N A_{ij}, \quad (\text{A19})$$

so that its Weyl transform is of the form:

$$a(1, \dots, N) = \sum_{i,j=1(i \neq j)}^N a_{ij}(i, j), \quad (\text{A20})$$

its average value may be written as

$$\bar{A}(t) = \int a_{12}(1, 2) f_2(1, 2; t) d1 d2 \quad (\text{A21})$$

with the two-point reduced Wigner function

$$f_2(1, 2; t) = N(N-1) \int \rho(1, 2, \dots, N; t) d3 \dots dN, \quad (\text{A22})$$

normalized to $N(N-1)$.

The two-point correlation function is defined as

$$c_2(1, 2; t) = f_2(1, 2; t) - f_1(1; t) f_1(2; t), \quad (\text{A23})$$

normalized to $-N$.

d. The reduced Wigner function for a perfect gas¹

The Wigner function for a mixed state is a weighted sum (A3) of Wigner functions (A4) for pure states. Often the density operator and hence also the Wigner function is a superposition of energy states, i.e. the index γ in (A1-4) labels the energy states. The wave functions corresponding to the eigenstates of the energy for an N -particle system have simple forms in the case of a perfect gas:

$$\psi(\mathbf{q}_1, \dots, \mathbf{q}_N; t) = \sqrt{\frac{n_1! n_2! n_3! \dots n_m!}{N!}} \sum_{\mathbf{P}} (\pm 1)^{\mathbf{P}} \{u_1(\mathbf{q}_1) u_1(\mathbf{q}_2) \dots u_1(\mathbf{q}_{n_1}) u_2(\mathbf{q}_{n_1+1}) \dots u_m(\mathbf{q}_N)\} e^{-(i/\hbar)Et}, \quad (\text{A24})$$

where the upper and lower sign refer to boson and fermion systems respectively. The orthonormal functions $u_k(\mathbf{q}_i)$ are one-particle eigenfunctions of the one-particle Hamiltonian for particle i with energy value E_k . In the product the eigenfunction u_k occurs n_k times (with n_k the occupation number of energy level k ; $\sum_{k=1}^m n_k = N$). In the fermion case n_k can only assume the values 0 or 1. The sum is extended over those permutations of the arguments \mathbf{q}_i of the functions u_k which yield different terms. The number of these permutations is therefore $N!/n_1!n_2! \dots n_m!$. The factor $(-1)^{\mathbf{P}}$ is plus or minus 1 for an even or odd permutation respectively. As a consequence of the orthonormality of the one-particle eigenfunctions the normalization of ψ is

¹ Cf. J. E. Moyal, Proc. Cambr. Phil. Soc. 45(1949)99.

guaranteed. The wave function ψ is an eigenfunction of the total Hamiltonian with eigenvalue $E = \sum_{k=1}^m n_k E_k$.

Let us now consider the Wigner function (A4) of the state (A24). We shall study only the reduced Wigner functions of the type (A18) and (A22). The one-point reduced Wigner function gets the form:

$$f_1(\mathbf{p}_1, \mathbf{q}_1) = h^{-3N} \frac{n_1! n_2! \dots n_m!}{N!} \sum_{\mathbf{P}} \sum_{\mathbf{P}'} (\pm 1)^{\mathbf{P}} (\pm 1)^{\mathbf{P}'}$$

$$\int d\mathbf{v}_1 \dots d\mathbf{v}_N d\mathbf{p}_2 \dots d\mathbf{p}_N d\mathbf{q}_2 \dots d\mathbf{q}_N \exp\left(\frac{i}{\hbar} \sum_{i=1}^N \mathbf{p}_i \cdot \mathbf{v}_i\right)$$

$$\mathbf{P}\{u_1(\mathbf{q}_1 - \frac{1}{2}\mathbf{v}_1) u_1(\mathbf{q}_2 - \frac{1}{2}\mathbf{v}_2) \dots u_m(\mathbf{q}_N - \frac{1}{2}\mathbf{v}_N)\}$$

$$\mathbf{P}'\{u_1^*(\mathbf{q}_1 + \frac{1}{2}\mathbf{v}_1) u_1^*(\mathbf{q}_2 + \frac{1}{2}\mathbf{v}_2) \dots u_m^*(\mathbf{q}_N + \frac{1}{2}\mathbf{v}_N)\}. \quad (\text{A25})$$

In order to evaluate this expression it is convenient to introduce ancillary functions defined as

$$f_{kl}(\mathbf{p}, \mathbf{q}) = h^{-3} \int d\mathbf{v} e^{(i/\hbar)\mathbf{p} \cdot \mathbf{v}} u_k(\mathbf{q} - \frac{1}{2}\mathbf{v}) u_l^*(\mathbf{q} + \frac{1}{2}\mathbf{v}). \quad (\text{A26})$$

As a consequence of the orthonormality of the u_k , this function has the property

$$\int d\mathbf{p} d\mathbf{q} f_{kl}(\mathbf{p}, \mathbf{q}) = \delta_{kl}. \quad (\text{A27})$$

With (A26) and (A27) one finds from (A25)

$$f_1(1) = \sum_{k=1}^m n_k f_{kk}(1), \quad (\text{A28})$$

where 1 stands for \mathbf{p}_1 and \mathbf{q}_1 .

In an analogous way one may derive the two-point reduced Wigner function (A22) that corresponds to the wave function (A24):

$$f_2(1, 2) = \sum_{k,l=1(k \neq l)}^m n_k n_l f_{kk}(1) f_{ll}(2) + \sum_{k=1}^m n_k (n_k - 1) f_{kk}(1) f_{kk}(2)$$

$$\pm \sum_{k,l=1(k \neq l)}^m n_k n_l f_{kl}(1) f_{lk}(2). \quad (\text{A29})$$

If the system is described by a mixture of energy states of the type (A24), one finds from (A3) that the one-point and two-point reduced Wigner functions are:

$$f_1(1) = \sum_k \bar{n}_k f_{kk}(1), \quad (\text{A30})$$

$$f_2(1, 2) = \sum_{k,l(k \neq l)} \overline{\bar{n}_k \bar{n}_l} f_{kk}(1) f_{ll}(2) + \sum_k \overline{n_k(n_k-1)} f_{kk}(1) f_{kk}(2) \pm \sum_{k,l(k \neq l)} \overline{\bar{n}_k \bar{n}_l} f_{kl}(1) f_{lk}(2), \quad (\text{A31})$$

where the bars denote weighted averages over the pure states γ with weights w_γ .

If one uses as the mixed state the grand-canonical ensemble¹ of energy states with temperature T one finds for the average occupation numbers

$$\bar{n}_k = \frac{1}{\xi e^{E_k/kT} \mp 1}, \quad (\text{A32})$$

where the constant ξ follows from $\sum_k \bar{n}_k = \bar{N}$. Furthermore one finds then for the other averages of occupation numbers which occur in (A31)²

$$\overline{\bar{n}_k \bar{n}_l} = \bar{n}_k \bar{n}_l, \quad (k \neq l), \quad (\text{A33})$$

$$\overline{n_k(n_k-1)} = (1 \pm 1)(\bar{n}_k)^2. \quad (\text{A34})$$

With the use of (A33) and (A34) the expression (A31) may be written as

$$f_2(1, 2) = \sum_{k,l} \bar{n}_k \bar{n}_l f_{kk}(1) f_{ll}(2) \pm \sum_{k,l} \bar{n}_k \bar{n}_l f_{kl}(1) f_{lk}(2), \quad (\text{A35})$$

where in the double sums the case $k = l$ is included. In this way both the one-point Wigner function (A30) and the two-point function (A35) have been expressed in terms of mean occupation numbers (A32) and the ancillary functions (A26).

By substituting (A30) into (A35) we obtain

$$f_2(1, 2) = f_1(1) f_1(2) \pm \sum_{k,l} \bar{n}_k \bar{n}_l f_{kl}(1) f_{lk}(2). \quad (\text{A36})$$

For the correlation function $c_2(1, 2)$, defined in (A23), we have thus found

$$c_2(1, 2) = \pm \sum_{k,l} \bar{n}_k \bar{n}_l f_{kl}(1) f_{lk}(2). \quad (\text{A37})$$

In order to obtain explicit expressions we must find values for the ancillary

¹ We prefer to use here the grand-canonical ensemble rather than the canonical ensemble in view of the fact that then the averages, occurring in (A30) and (A31), may be found in a simple way. Since in this ensemble the total number of particles is not fixed, one finds for the normalization of the reduced Wigner functions $f_1(1)$, $f_2(1, 2)$ and $c_2(1, 2)$ the values \bar{N} , $\bar{N}(\bar{N}-1)$ and $\bar{N}(\bar{N}-1) - (\bar{N})^2$ instead of N , $N(N-1)$ and $-N$ respectively. This follows directly from (A30) and (A31) with (A27).

² Excluding the ground level $k = 0$ for the Bose-Einstein case.

functions $f_{kl}(1)$ (A26). We choose for the functions $u_k(\mathbf{q})$ the plane waves

$$u_{\mathbf{n}}(\mathbf{q}) = V^{-\frac{1}{2}} e^{(2\pi i/a)\mathbf{n}\cdot\mathbf{q}}, \quad (\text{A38})$$

where the components n_x , n_y and n_z of the vector \mathbf{n} may assume the values $0, \pm 1, \pm 2, \dots$. These plane waves are eigenfunctions of the free particle Hamiltonian with eigenvalues

$$E_{\mathbf{n}} = \frac{\hbar^2 \mathbf{n}^2}{2ma^2}. \quad (\text{A39})$$

The plane waves (A38) are chosen such that periodic boundary conditions involving a cube with edge a and volume $V \equiv a^3$ are satisfied. Then according to (A26) we get

$$f_{\mathbf{n}\mathbf{n}'} = V^{-1} e^{(2\pi i/a)(\mathbf{n}-\mathbf{n}')\cdot\mathbf{q}} \delta \left\{ \mathbf{p} - \frac{\hbar(\mathbf{n}+\mathbf{n}')}{2a} \right\}. \quad (\text{A40})$$

This is to be inserted into (A30) with (A32). If the summation over the vector \mathbf{n} is replaced by an integral by introducing the integration variable $\mathbf{p}' = \hbar\mathbf{n}/a$, one obtains

$$f_1(\mathbf{p}, \mathbf{q}) = h^{-3} \int d\mathbf{p}' \bar{n}(\mathbf{p}') \delta(\mathbf{p} - \mathbf{p}') = h^{-3} \bar{n}(\mathbf{p}). \quad (\text{A41})$$

Furthermore one finds for $f_2(1, 2)$ given by (A36) with (A32):

$$\begin{aligned} f_2(\mathbf{p}_1, \mathbf{q}_1, \mathbf{p}_2, \mathbf{q}_2) &= h^{-6} \bar{n}(\mathbf{p}_1) \bar{n}(\mathbf{p}_2) \\ &\pm h^{-6} \int d\mathbf{p}' d\mathbf{p}'' \bar{n}(\mathbf{p}') \bar{n}(\mathbf{p}'') e^{(i/\hbar)(\mathbf{p}'-\mathbf{p}'')\cdot(\mathbf{q}_1-\mathbf{q}_2)} \\ &\delta \left(\mathbf{p}_1 - \frac{\mathbf{p}'+\mathbf{p}''}{2} \right) \delta \left(\mathbf{p}_2 - \frac{\mathbf{p}'+\mathbf{p}''}{2} \right) \\ &= h^{-6} \bar{n}(\mathbf{p}_1) \bar{n}(\mathbf{p}_2) \pm h^{-6} \delta(\mathbf{p}_1 - \mathbf{p}_2) \int d\mathbf{p}' \bar{n}(\mathbf{p}_1 + \frac{1}{2}\mathbf{p}') \bar{n}(\mathbf{p}_1 - \frac{1}{2}\mathbf{p}') e^{(i/\hbar)\mathbf{p}'\cdot(\mathbf{q}_1-\mathbf{q}_2)}, \end{aligned} \quad (\text{A42})$$

so that the correlation function (A37) becomes

$$\begin{aligned} c_2(\mathbf{p}_1, \mathbf{q}_1, \mathbf{p}_2, \mathbf{q}_2) &= \pm h^{-6} \delta(\mathbf{p}_1 - \mathbf{p}_2) \int d\mathbf{p}' \bar{n}(\mathbf{p}_1 + \frac{1}{2}\mathbf{p}') \bar{n}(\mathbf{p}_1 - \frac{1}{2}\mathbf{p}') e^{(i/\hbar)\mathbf{p}'\cdot(\mathbf{q}_1-\mathbf{q}_2)}. \end{aligned} \quad (\text{A43})$$

The mean occupation numbers occurring in this expression are almost constants if the integration variable changes by an amount which is smaller

than $(2\pi mkT)^{\frac{1}{2}}$. Furthermore the exponential oscillates rapidly in this interval if $|\mathbf{q}_1 - \mathbf{q}_2|$ is large compared to the thermal wave length $h(2\pi mkT)^{-\frac{1}{2}}$. Hence one may conclude that the range of the Wigner correlation function (A43) as a function of $|\mathbf{q}_1 - \mathbf{q}_2|$ is of the order of the thermal wave length.

The Hamilton operator for a system of composite particles in an external field

The non-relativistic Hamilton operator for a set of charged particles ki grouped into stable entities k is given by the expression (VI.1) (compare also the classical Hamiltonian (II.A26)):

$$\begin{aligned}
 H_{\text{op}}(\mathbf{P}_{ki,\text{op}}, \mathbf{R}_{ki,\text{op}}, t) &= \sum_{k,i} \frac{\mathbf{P}_{ki,\text{op}}^2}{2m_{ki}} \\
 &+ \sum_k \sum_{i,j(i \neq j)} \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki,\text{op}} - \mathbf{R}_{kj,\text{op}}|} + \sum_{k,l(k \neq l)} \sum_{i,j} \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki,\text{op}} - \mathbf{R}_{lj,\text{op}}|} \\
 &+ \sum_{k,i} e_{ki} \left[\varphi_e(\mathbf{R}_{ki,\text{op}}, t) - \frac{1}{2} c^{-1} \left\{ \frac{\mathbf{P}_{ki,\text{op}}}{m_{ki}} \cdot \mathbf{A}_e(\mathbf{R}_{ki,\text{op}}, t) \right\} \right], \quad (\text{A44})
 \end{aligned}$$

with m_{ki} the mass of particle ki , e_{ki} its charge, $\mathbf{R}_{ki,\text{op}}$ its coordinate operator, $\mathbf{P}_{ki,\text{op}}$ its momentum operator. Furthermore φ_e and \mathbf{A}_e are scalar and vector potentials of the external electromagnetic field. The last term contains a scalar product denoted by a dot, and an anticommutator, denoted by curly brackets and a comma. In analogy with the classical treatment one may introduce new coordinate and momentum operators for the particles belonging to group k , such that the new coordinate operators are the centre of mass operator and the relative coordinate operators of the constituent particles ki with respect to this centre of mass operator:

$$\begin{aligned}
 \mathbf{q}_{ki,\text{op}} &= \mathbf{R}_{ki,\text{op}} - \mathbf{R}_{k,\text{op}} \equiv \mathbf{R}_{ki,\text{op}} - \sum_{j=1}^f (m_{kj}/m_k) \mathbf{R}_{kj,\text{op}}, \quad (i = 1, \dots, f-1), \\
 \mathbf{q}_{kf,\text{op}} &= \mathbf{R}_{k,\text{op}} \equiv \sum_{j=1}^f (m_{kj}/m_k) \mathbf{R}_{kj,\text{op}}, \\
 \mathbf{p}_{ki,\text{op}} &= \mathbf{P}_{ki,\text{op}} - (m_{kj}/m_{kf}) \mathbf{P}_{kf,\text{op}}, \quad (i = 1, \dots, f-1), \\
 \mathbf{p}_{kf,\text{op}} &= \mathbf{P}_{k,\text{op}} \equiv \sum_{i=1}^f \mathbf{P}_{ki,\text{op}}.
 \end{aligned} \quad (\text{A45})$$

If one inverts these relations one gets

$$\mathbf{R}_{ki,op} = \mathbf{R}_{k,op} + (1 - \delta_{if}) \mathbf{q}_{ki,op} - \delta_{if} \sum_{j=1}^{f-1} (m_{kj}/m_{kf}) \mathbf{q}_{kj,op}, \quad (\text{A46})$$

$$\mathbf{P}_{ki,op} = (m_{ki}/m_k) \mathbf{P}_{k,op} + (1 - \delta_{if}) \mathbf{p}_{ki,op} - (m_{ki}/m_k) \sum_{j=1}^{f-1} \mathbf{p}_{kj,op}.$$

The transformed Hamilton operator is obtained by insertion of (A46) into (A44). Then one obtains for the Weyl transform of the new Hamilton operator (cf. the classical expression (II.A29)):

$$\begin{aligned} H_{op}(\mathbf{p}_{op}, \mathbf{q}_{op}, t) &\rightleftharpoons \sum_k \left(\frac{\mathbf{P}_k^2}{2m_k} + \sum_{i=1}^{f-1} \frac{\mathbf{p}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{\mathbf{p}_{ki} \cdot \mathbf{p}_{kj}}{2m_k} \right) \\ &+ \sum_k \sum_{i,j=1}^f \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{kj}(\mathbf{q})|} + \sum_{k,l(k \neq l)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{lj}(\mathbf{q})|} \\ &+ \sum_k e_k \left\{ \varphi_e(\mathbf{R}_k, t) - c^{-1} \frac{\mathbf{P}_k}{m_k} \cdot \mathbf{A}_e(\mathbf{R}_k, t) \right\} \\ &+ \sum_k \sum_{i=1}^f e_{ki} \left[\{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{kj} \} \cdot \nabla_k \left\{ \varphi_e(\mathbf{R}_k, t) - c^{-1} \frac{\mathbf{P}_k}{m_k} \cdot \mathbf{A}_e(\mathbf{R}_k, t) \right\} \right. \\ &- c^{-1} \left. \left(\frac{\mathbf{p}_{ki}(\mathbf{p})}{m_{ki}} - \frac{\mathbf{P}_k}{m_k} \right) \cdot \mathbf{A}_e(\mathbf{R}_k, t) \right. \\ &- c^{-1} \left. \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_k \} \cdot \nabla_k \mathbf{A}_e(\mathbf{R}_k, t) \cdot \left(\frac{\mathbf{p}_{ki}(\mathbf{p})}{m_{ki}} - \frac{\mathbf{P}_k}{m_k} \right) \right], \quad (\text{A47}) \end{aligned}$$

up to terms with derivatives of the potentials. At the right-hand side the symbols $\mathbf{R}_{ki}(\mathbf{q})$ and $\mathbf{P}_{ki}(\mathbf{p})$ stand for the right-hand sides of (A46) but without the index *op*. Since the Weyl correspondence is invariant under a linear transformation of coordinates and momenta (v. problem 2 of chapter VI), the correspondence sign may be understood either as a Weyl correspondence with respect to the old coordinates and momenta \mathbf{R}_{ki} , \mathbf{P}_{ki} or with respect to the new coordinates (A45). A second, non-linear transformation of coordinates and momenta as employed in the classical treatment of appendix II of chapter II, will not be performed here, because the Weyl correspondence is not invariant under that non-linear transformation.

Let us consider the Weyl transform K defined as

$$K \equiv \sum_k \sum_{i=1}^f \frac{1}{2} m_{ki} (\hat{\partial}_{iP} \mathbf{R}_{ki})^2, \quad (\text{A48})$$

where the symbol ∂_{iP} stands for the Poisson bracket (cf. (VI.72))

$$\partial_{iP} a = \{a, H\}_P \quad (\text{A49})$$

for a independent of t . The function H is the Weyl transform of the Hamilton operator (A44) or alternatively the right-hand side of (A47). According to (A45) we may write (A48) as

$$K = \sum_k \frac{1}{2} m_k (\hat{\partial}_{iP} \mathbf{R}_k)^2 + \sum_k \left\{ \sum_{i=1}^{f-1} \frac{1}{2} m_{ki} (\partial_{iP} \mathbf{q}_{ki})^2 + \sum_{i,j=1}^{f-1} \frac{1}{2} \frac{m_{ki} m_{kj}}{m_{kf}} (\partial_{iP} \mathbf{q}_i) \cdot (\partial_{iP} \mathbf{q}_{kj}) \right\}. \quad (\text{A50})$$

The Poisson brackets may be evaluated in terms of either the old coordinates and momenta (\mathbf{R}_{ki} , \mathbf{P}_{ki}) or the new variables (\mathbf{q}_{ki} , \mathbf{p}_{ki}). If one chooses the latter set of variables and for the Weyl transform of the Hamilton operator the right-hand side of (A47) one finds for (A50), with $e_k = \sum_i e_{ki}$:

$$\begin{aligned} K &= \sum_k \left[\frac{\mathbf{P}_k^2}{2m_k} - \frac{c^{-1} e_k}{m_k} \mathbf{P}_k \cdot \mathbf{A}_e(\mathbf{R}_k, t) \right. \\ &- c^{-1} \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_k \} \cdot \nabla_k \frac{\mathbf{P}_k}{m_k} \cdot \mathbf{A}_e(\mathbf{R}_k, t) \left. \right] \\ &+ \sum_k \left[\sum_{i=1}^{f-1} \frac{\mathbf{p}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{\mathbf{p}_{ki} \cdot \mathbf{p}_{kj}}{2m_k} - c^{-1} \sum_{i=1}^f e_{ki} \left(\frac{\mathbf{p}_{ki}(\mathbf{p})}{m_{ki}} - \frac{\mathbf{P}_k}{m_k} \right) \cdot \mathbf{A}_e(\mathbf{R}_k, t) \right. \\ &- c^{-1} \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_k \} \cdot \nabla_k \mathbf{A}_e(\mathbf{R}_k, t) \cdot \left(\frac{\mathbf{p}_{ki}(\mathbf{p})}{m_{ki}} - \frac{\mathbf{P}_k}{m_k} \right) \left. \right]. \quad (\text{A51}) \end{aligned}$$

If this is used in the right-hand side of (A47), one finds

$$\begin{aligned} H_{op}(\mathbf{p}_{op}, \mathbf{q}_{op}, t) &\rightleftharpoons K + \sum_k \sum_{i,j=1}^f \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{kj}(\mathbf{q})|} \\ &+ \sum_{k,l(k \neq l)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{lj}(\mathbf{q})|} \\ &+ \sum_k e_k \varphi_e(\mathbf{R}_k, t) + \sum_k \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_k \} \cdot \nabla_k \varphi_e(\mathbf{R}_k, t). \quad (\text{A52}) \end{aligned}$$

If the external electromagnetic fields \mathbf{E}_e and \mathbf{B}_e are uniform and time-independent, one may choose as potentials $\varphi_e(\mathbf{R}, t)$ and $\mathbf{A}_e(\mathbf{R}, t)$:

$$\begin{aligned} \varphi_e(\mathbf{R}) &= -\mathbf{R} \cdot \mathbf{E}_e, \\ \mathbf{A}_e(\mathbf{R}) &= \frac{1}{2} \mathbf{B}_e \wedge \mathbf{R}, \end{aligned} \quad (\text{A53})$$

which are time-independent¹. If these expressions are substituted into the right-hand side of (A47) one finds

$$\begin{aligned}
H_{\text{op}}(\mathbf{p}_{\text{op}}, \mathbf{q}_{\text{op}}, t) \rightleftharpoons & \sum_k \left(\frac{\mathbf{P}_k^2}{2m_k} + \sum_{i=1}^{f-1} \frac{\mathbf{p}_{ki}^2}{2m_{ki}} - \sum_{i,j=1}^{f-1} \frac{\mathbf{p}_{ki} \cdot \mathbf{p}_{kj}}{2m_k} \right) \\
& + \sum_k \sum_{i,j=1(i \neq j)}^f \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{kj}(\mathbf{q})|} \\
& + \sum_{k,l(k \neq l)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{lj}(\mathbf{q})|} - \sum_k \left\{ e_k \mathbf{R}_k \cdot \left(\mathbf{E}_c + \frac{1}{2} c^{-1} \frac{\mathbf{P}_k}{m_k} \wedge \mathbf{B}_c \right) \right. \\
& \left. + \bar{\boldsymbol{\mu}}_k^{(1)} \cdot \left(\mathbf{E}_c + \frac{1}{2} c^{-1} \frac{\mathbf{P}_k}{m_k} \wedge \mathbf{B}_c \right) + \frac{1}{2} c^{-1} \partial_{i\mathbf{p}} \bar{\boldsymbol{\mu}}_k^{(1)} \cdot (\mathbf{B}_c \wedge \mathbf{R}_k) + \bar{\mathbf{v}}_k^{(1)} \cdot \mathbf{B}_c \right\} \quad (\text{A54})
\end{aligned}$$

with the abbreviations (cf. (II.A33))

$$\bar{\boldsymbol{\mu}}_k^{(1)}(\mathbf{q}) = \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{q}_{kf} \}, \quad (\text{A55})$$

$$\bar{\mathbf{v}}_k^{(1)}(\mathbf{p}, \mathbf{q}) = \frac{1}{2} c^{-1} \sum_{i=1}^f e_{ki} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{q}_{kf} \} \wedge \left\{ (1 - \delta_{if}) \frac{\mathbf{p}_{ki}}{m_{ki}} - \sum_{j=1}^{f-1} \frac{\mathbf{p}_{kj}}{m_k} \right\}.$$

These quantities are the Weyl transforms of the electric and magnetic dipole moment operators. They are indeed equal to the case $n = 1$ of (VI.94), since $\mathbf{q}_{kf} \equiv \mathbf{R}_k$ and since, up to order c^0 , one has

$$(1 - \delta_{if}) \frac{\mathbf{p}_{ki}}{m_{ki}} - \sum_{j=1}^{f-1} \frac{\mathbf{p}_{kj}}{m_k} = \partial_{i\mathbf{p}} \{ \mathbf{R}_{ki}(\mathbf{q}) - \mathbf{q}_{kf} \}. \quad (\text{A56})$$

Finally one obtains for (A52):

$$\begin{aligned}
H_{\text{op}}(\mathbf{p}_{\text{op}}, \mathbf{q}_{\text{op}}, t) \rightleftharpoons & K + \sum_k \sum_{i,j=1(i \neq j)}^f \frac{e_{ki} e_{kj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{kj}(\mathbf{q})|} \\
& + \sum_{k,l(k \neq l)} \sum_{i,j=1}^f \frac{e_{ki} e_{lj}}{8\pi |\mathbf{R}_{ki}(\mathbf{q}) - \mathbf{R}_{lj}(\mathbf{q})|} - \sum_k e_k \mathbf{R}_k \cdot \mathbf{E}_c - \sum_k \bar{\boldsymbol{\mu}}_k^{(1)} \cdot \mathbf{E}_c. \quad (\text{A57})
\end{aligned}$$

Whereas the form (A55) shows explicitly the dependence on the external magnetic field, this dependence is now hidden in the quantity K .

¹ Other time-independent potentials, which might be used as well in the Hamiltonian, are of the form

$$\begin{aligned}
\varphi'_e &= -\mathbf{R} \cdot \mathbf{E}_c + \chi \\
\mathbf{A}'_e &= \frac{1}{2} \mathbf{B}_c \wedge \mathbf{R} + \nabla \psi(\mathbf{R}),
\end{aligned}$$

where χ and $\psi(\mathbf{R})$ may depend also on the external fields. Although the Hamiltonian becomes more complicated then, the final results, derived in the main text, remain the same.

Deformations and free energy in quantum theory

In quantum statistical mechanics the free energy F^* of a system of atoms described by a canonical ensemble with temperature T is given by the expression

$$e^{-F^*/kT} = \text{Tr} \{ \exp(-H_{\text{op}}^{\text{W}}/kT) \}. \quad (\text{A58})$$

Here the total Hamilton operator H_{op}^{W} is the sum of the Hamilton operator H_{op} and the wall potential operator U_{op}^{W} :

$$U_{\text{op}}^{\text{W}} = \sum_k U_{k,\text{op}}^{\text{W}}(\mathbf{R}_{k,\text{op}}), \quad (\text{A59})$$

where $\mathbf{R}_{k,\text{op}}$ is the centre of mass operator of atom k and the sum is extended over all atoms of the system. The wall potential operator $U_{k,\text{op}}^{\text{W}}$ has the same eigenfunctions as $\mathbf{R}_{k,\text{op}}$ and eigenvalues ∞ or 0 if the eigenvalues of $\mathbf{R}_{k,\text{op}}$ denote positions outside or inside the boundary of the system respectively.

If the position of the boundary is deformed according to the formula:

$$\mathbf{R}^{\text{W}'} = \{ \mathbf{U} + \delta \boldsymbol{\epsilon}(\mathbf{R}^{\text{W}}) \} \cdot \mathbf{R}^{\text{W}}, \quad (\text{A60})$$

with \mathbf{U} the unit tensor and $\delta \boldsymbol{\epsilon}(\mathbf{R}^{\text{W}})$ the deformation tensor, the wall potential becomes:

$$U_{\text{op}}^{\text{W}'} = \sum_k U_{k,\text{op}}^{\text{W}} [\{ \mathbf{U} - \delta \boldsymbol{\epsilon}(\mathbf{R}_{k,\text{op}}) \} \cdot \mathbf{R}_{k,\text{op}}]. \quad (\text{A61})$$

Deformation of the boundary leads to a change of the free energy:

$$\delta_\epsilon F^* = -kT e^{F^*/kT} \delta \text{Tr} \{ \exp(-H_{\text{op}}^{\text{W}}/kT) \}, \quad (\text{A62})$$

according to (A58). We now use the identity (81) with (82) for the derivative of an exponential operator, so as to derive

$$\delta_\epsilon F^* = \text{Tr} \{ e^{(F^* - H_{\text{op}}^{\text{W}})/kT} \delta U_{\text{op}}^{\text{W}} \}, \quad (\text{A63})$$

where we used the fact that the traces of the commutators occurring here vanish and where $\delta U_{\text{op}}^{\text{W}}$ stands for $U_{\text{op}}^{\text{W}'} - U_{\text{op}}^{\text{W}}$. With the insertion of (A61) we obtain for (A63)

$$\delta_\epsilon F^* = -\text{Tr} \{ e^{(F^* - H_{\text{op}}^{\text{W}})/kT} \sum_k \mathbf{R}_{k,\text{op}} \cdot \delta \boldsymbol{\epsilon}(\mathbf{R}_{k,\text{op}}) \cdot \nabla_k U_{k,\text{op}}^{\text{W}}(\mathbf{R}_{k,\text{op}}) \}. \quad (\text{A64})$$

Writing this average in terms of the Wigner function of the canonical ensemble we get

$$\delta_\varepsilon F^* = - \int \sum_k \mathbf{R}_k \cdot \delta \tilde{\mathbf{e}}(\mathbf{R}_k) \cdot \nabla_k U_k^W(\mathbf{R}_k) \rho(1, \dots, N) d1 \dots dN. \quad (\text{A65})$$

Now according to (13) and the stationarity of the canonical ensemble

$$\begin{aligned} 0 &= \frac{\partial}{\partial t} \int \sum_k \mathbf{P}_k \cdot \delta \mathbf{e}(\mathbf{R}_k) \cdot \mathbf{R}_k \rho(1, \dots, N) d1 \dots dN \\ &= \int \sum_k \{H^W, \mathbf{P}_k \cdot \delta \mathbf{e}(\mathbf{R}_k) \cdot \mathbf{R}_k\}_P \rho(1, \dots, N) d1 \dots dN, \quad (\text{A66}) \end{aligned}$$

where H^W is the Weyl transform of the total Hamiltonian H_{op}^W and where Poisson brackets appear in the last member. Splitting H^W into the Weyl transform H of the Hamilton operator and U^W of the wall potential operator, and evaluating the Poisson brackets we get for (A66)

$$\begin{aligned} &\int \sum_k \mathbf{R}_k \cdot \delta \tilde{\mathbf{e}}(\mathbf{R}_k) \cdot \nabla_k U_k^W(\mathbf{R}_k) \rho(1, \dots, N) d1 \dots dN \\ &= \int \sum_k \left\{ \mathbf{P}_k \cdot \delta \mathbf{e}(\mathbf{R}_k) \cdot \frac{\partial H}{\partial \mathbf{P}_k} - \frac{\partial H}{\partial \mathbf{R}_k} \cdot \delta \mathbf{e}(\mathbf{R}_k) \cdot \mathbf{R}_k \right\} \rho(1, \dots, N) d1 \dots dN, \quad (\text{A67}) \end{aligned}$$

where the deformation gradient tensor $\delta \mathbf{e}$, defined in (II.A51) has been used. Substituting this result into (A65) we get finally

$$\delta_\varepsilon F^* = - \int \sum_k \left\{ \mathbf{P}_k \cdot \delta \mathbf{e}(\mathbf{R}_k) \cdot \frac{\partial H}{\partial \mathbf{P}_k} - \frac{\partial H}{\partial \mathbf{R}_k} \cdot \delta \mathbf{e}(\mathbf{R}_k) \cdot \mathbf{R}_k \right\} \rho(1, \dots, N) d1 \dots dN. \quad (\text{A68})$$

For uniform deformations $\delta \mathbf{e} = \delta \mathbf{e}$, so that one has for the change of the free energy

$$\delta_\varepsilon F^* = \mathbf{A} : \delta \mathbf{e} \quad (\text{A69})$$

with the tensor \mathbf{A} given by

$$\mathbf{A} = - \int \sum_k \left(\frac{\partial H}{\partial \mathbf{P}_k} \mathbf{P}_k - \mathbf{R}_k \frac{\partial H}{\partial \mathbf{R}_k} \right) \rho(1, \dots, N) d1 \dots dN, \quad (\text{A70})$$

which proves formula (97) of the main text.

PROBLEMS

1. Prove that (56) is the average of the operator given in (57). Show first, with the help of the expression (VI.61) for the Weyl transform of the Hamiltonian, that one has

$$m_{ki} \partial_{tP} \mathbf{R}_{ki} = \mathbf{P}_{ki} - c^{-1} e_{ki} \mathbf{A}_e(\mathbf{R}_{ki}, t),$$

so that one finds for $\mathbf{v}_k \equiv \partial_{tP} \mathbf{R}_k$:

$$\mathbf{v}_k = \frac{1}{m_k} \sum_i \{ \mathbf{P}_{ki} - c^{-1} e_{ki} \mathbf{A}_e(\mathbf{R}_{ki}, t) \}.$$

2. Consider a particle in an external electromagnetic field. Its wave function satisfies the Schrödinger equation $H_{\text{op}} \psi(\mathbf{R}, t) = -(\hbar/i) \partial \psi(\mathbf{R}, t) / \partial t$ with the Hamilton operator up to order c^{-1}

$$H_{\text{op}}(\mathbf{P}_{\text{op}}, \mathbf{R}_{\text{op}}) = \frac{\mathbf{P}_{\text{op}}^2}{2m} - \frac{e}{2mc} \{ \mathbf{P}_{\text{op}} \cdot \mathbf{A}_e(\mathbf{R}_{\text{op}}, t) \} + e\varphi_e(\mathbf{R}_{\text{op}}, t).$$

Show that the transformation

$$\psi'(\mathbf{R}', t') = \exp \left\{ \frac{i}{\hbar} (m\mathbf{V} \cdot \mathbf{R} + \frac{1}{2} mV^2 t) \right\} \psi(\mathbf{R}, t)$$

of the wave function with respect to a Galilei transformation (66) leaves the Schrödinger equation invariant, at least up to order c^{-1} . Use to that end the transformation rules (II.23) (which imply $\mathbf{P}'_{\text{op}} = \mathbf{P}_{\text{op}}$) and the transformation properties of the potentials (cf. (II.27))

$$\mathbf{A}'_e(\mathbf{R}', t') = \mathbf{A}_e(\mathbf{R}, t) + c^{-1} \mathbf{V} \varphi_e(\mathbf{R}, t),$$

$$\varphi'_e(\mathbf{R}', t') = \varphi_e(\mathbf{R}, t) + c^{-1} \mathbf{V} \cdot \mathbf{A}_e(\mathbf{R}, t).$$

The transformed Hamiltonian is thus

$$\mathbf{H}'_{\text{op}}(\mathbf{P}'_{\text{op}}, \mathbf{R}'_{\text{op}}) = H_{\text{op}}(\mathbf{P}_{\text{op}}, \mathbf{R}_{\text{op}}) + c^{-1} e\mathbf{V} \cdot \mathbf{A}_e(\mathbf{R}_{\text{op}}, t).$$

Since $\mathbf{P}'_{\text{op}} = \mathbf{P}_{\text{op}}$ and $\mathbf{R}'_{\text{op}} = \mathbf{R}_{\text{op}} + \mathbf{V}t$ one finds (68).

Prove furthermore (69) from the transformation of the wave function.

