Electron and nuclear pressures in electron-nucleus mixtures

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It is shown for an electron-nucleus mixture that the electron and nuclear pressures are defined clearly and simply by the virial theorem; the total pressure of this system is a sum of these two pressures. The electron pressure is different from the conventional electron pressure being expressed as the sum of two times of kinetic energy and the potential energy in that the nuclear virial term is subtracted; this fact is exemplified by several kinds of definitions for the electron pressure enumerated in this work. The conventional definition of the electron pressure in terms of the nuclear virial term is shown inappropriate. Similar remarks are made about the definition of the stress tensor in this mixture. It is also demonstrated that both of the electron and nuclear pressures become zero at the same time for a metal in the vacuum, in contrast to the conventional viewpoint that the zero pressure is realized by a result of the cancellation between the electron and nuclear pressures, each of which is not zero. On the basis of these facts, a simple equation of states for liquid metals is derived, and examined numerically for liquid alkaline metals by use of the quantum hypernetted chain equation and the Ashcroft model potential.

\section{Introduction}

In order to determine the properties of solids, liquid metals and plasmas as electron-nucleus mixtures, the nuclei (ions) are usually treated as classical particles, which are considered as giving an external potential for the electrons: as a result, we can apply the density-functional (DF) theory to this inhomogeneous electrons. Thus, the DF theory provides the inhomogeneous properties of the electrons under this external potential. Therefore, some problems occur to determine homogeneous quantities of an electron-nucleus mixture including the nuclear contribution from the results of the DF theory, where the nuclei appear only as providing an external potential. Such an example of problems occurs in the determination of the total pressure of electron-nucleus mixtures on the basis of the DF theory. The electron pressure is frequently discussed from the DF theory; nevertheless, the term, ‘electron pressure’ $P_e$, is differently used in two ways in its meaning. Some investigators\textsuperscript{1,2}) take the electron pressure $P_e$ for the electrons confined in a volume $V$ together with the fixed nuclei at the positions $\{R_\alpha\}$ to be $3P_eV = 2T_e + U_e$ in terms of the exact kinetic and potential energies, $T_e$ and $U_e$, respectively. On the other hand, many kinds of definitions for the electron pressure lead to an expression $3P_eV = 2T_e + U_e - \sum_\alpha R_\alpha \cdot F_\alpha$ with use of the force $F_\alpha$ on $\alpha$-nucleus, as will be shown in this work. This difference is not only a problem of the definition, since the total pressure of an electron-nucleus mixture as a homogeneous system is to be determined from the electron pressure in conjunction with the nuclear contribution: the definition of electron pressure should be consistent with this purpose, as will be done in this

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work. Therefore, it is important to see the meaning of the electron pressure in the calculation of the total pressure taking account of the nuclear contribution.

Following Slater,\(^3\) many investigators\(^1,2,4\) have identified the electron pressure with the total force on the nuclei; \(3\bar{P}_e V = \sum R_a \cdot F_a\). As a consequence of this definition which leads to the relation \(3\bar{P}_e V = 2T_e + U_e\), the 'electron pressure' becomes different from others as mentioned above. Similarly, the same problem was seen in the definition of the stress tensors\(^4\) in terms of the total force on the nuclei. This definition of \(\bar{P}_e\) is based on the assumption: an electron-nucleus mixture confined in a volume \(V\) by wall potentials, \(U_{ele}^w\) and \(U_{nuc}^w\), for the electrons and the nuclei, respectively, is thermodynamically identical with the mixture with only the nuclei confined in \(V\) by \(U_{nuc}^w\), since in the latter system the electrons seem to spill out outside the nuclei a distance only on an atomic scale even if \(U_{ele}^w = 0\). In this work, we will examine the validity of this assumption with use of the virial theorem which leads to a definition of the electron pressure in a more general form. From this new definition of the electron pressure, the total pressure of an electron-nucleus mixture is shown to be represented as a sum of the electron and nuclear pressures.

Also, we can give an important remark about the fact that the pressure in solids or liquid metals becomes zero in the vacuum; it is a standard viewpoint\(^5,6\) that the electron pressure is negative because of the electrons yielding a main part of cohesive energy, while the nuclear pressure is positive, and the total pressure becomes zero as a result of cancellation between two pressures in the vacuum. Contrary to this assertion, the total pressure becomes zero, since both the electron and nuclear pressures are zero at the same time in the vacuum, as we will see. In this work, we discuss on these problems from fundamental and simple virial relations.

Based on the fact that the total pressure of an electron-nucleus mixture is a sum of the electron and nuclear pressures, we obtain a simpler pressure formula for a liquid metal, where the effective interaction among nuclei (ions) are approximately represented by a pair interaction; the nuclear pressure is expressed in the virial form using this pair interaction and the radial distribution function. On the other hand, the electron pressure in a simple metal may be described by the jellium model. However, the electron pressure determined from the jellium model becomes zero only at the electron density of \(r_s \approx 4\) and the jellium surface energy becomes negative for \(r_s \approx 2\), while the jellium bulk modulus is negative at \(r_s \approx 6\). These drawbacks of the jellium model are rectified by the stabilized jellium (SJ) model\(^7\) (or the ideal metal model\(^8,9\)), where an infinitesimally thin dipole layer is added to the surface of the uniform background in the jellium; this dipole layer produces a uniform field in the jellium to make it stable at any metallic densities. On use of this SJ model to obtain an electron pressure expression, we derived a pressure formula for a simple liquid metal in the present work.

In the next section, we show that the electron and nuclear pressures are clearly defined on the basis of the simple and fundamental virial theorem, and construct three systems by changing the wall potentials confining the electrons and the nuclei in a finite volume. Based on these systems, we make several statements about the pressures for an electron-nucleus mixture. Similar remarks are made about the definition of the stress tensors for this mixture in \(\S3\). In \(\S4\) we enumerate several
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kinds of the definitions of the electron pressures proposed up to date. Equation of
states (EOS) for liquid metals is set up in §5.1; a numerical examination of this EOS
is performed in §5.2. The last section is devoted to summary and discussion. In
Appendix A the electron pressure formula is derived from the internal energy by
performing a volume derivative in the framework of the DF theory.

§2. Virial theorem for an electron-nucleus mixture

The Hamiltonian for an electron-nucleus mixture is represented by

\[ \hat{H} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \sum_\alpha \frac{\hat{p}_\alpha^2}{2M_\alpha} + \hat{U}(\{\hat{r}_i\}, \{\hat{R}_\alpha\}) \equiv \hat{T}_e + \hat{T}_N + \hat{U}, \quad (2.1) \]

where the coordinates and momenta of the electrons are denoted by \{\hat{r}_i, \hat{p}_i\} and
those of the nuclei by \{\hat{R}_\alpha, \hat{P}_\alpha\} with the Coulomb interactions between particles

\[ \hat{U} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\hat{r}_i - \hat{r}_j|} - \sum_{i,\alpha} \frac{Z_e^2}{|\hat{r}_i - \hat{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_e^2}{|\hat{R}_\alpha - \hat{R}_\beta|}. \quad (2.2) \]

This Coulomb potential \( \hat{U} \) of an electron-nucleus mixture satisfies the following op-
erator relation

\[ \hat{U} = - \sum_i \hat{r}_i \cdot \nabla_i \hat{U} - \sum_\alpha \hat{R}_\alpha \cdot \nabla_\alpha \hat{U}. \quad (2.3) \]

 Afterwards when the nuclei are regarded as classical particles, we use the symbols
\{\hat{R}_\alpha, \hat{P}_\alpha\} instead of \{\hat{r}_i, \hat{p}_i\}. In the standard approach to homogeneous liquid
and solid metals, it is commonly assumed that the nuclei are treated as classical
particles (or in the adiabatic approximation), and the electrons are considered as
an inhomogeneous electron system under the external potential \( U_{ex} \) caused by the
nuclei fixed at their equilibrium positions. Here, it is important in treating an
electron-nucleus mixture to recognize that there are four stages of approximations
to the nuclear behaviour: (i) the nuclear mass is approximated as infinite, where the
external potential \( U_{ex} \) is determined uniquely from a nuclear configuration, since the
nuclei do not move but remain to stay at their equilibrium positions; (ii) the nuclei
are approximated as classical particles in the sense that its position and momentum
are commutable; (iii) the nuclei are regarded as quantum particles, but can be treated
in the adiabatic approximation; and finally (iv) the nuclei can not be treated in the
adiabatic approximation. Therefore, we can apply the DF theory to the electrons
in the electron-nucleus mixture without any approximation, if the nuclear mass is
taken to be infinite.

Generally, the thermodynamic pressure \( P \) of an inhomogeneous system caused
by an external potential \( U_{ex}(r) \) is clearly defined in terms of free energy \( F \) or internal
energy \( E \),

\[ P = - \frac{\partial F}{\partial V} \bigg|_{TNU_{ex}(r)} = - \frac{\partial E}{\partial V} \bigg|_{SNU_{ex}(r)}. \quad (2.4) \]
under the condition that the volume parameter $V$ of particles confined by a wall potential $U_w(r)$ remains to specify the state as a natural variable when the external potential $U_{\text{ex}}(r)$ is imposed, as is described in detail.\[^{10}\] In addition to the thermodynamic pressure, there is another ‘kinetic’ definition of the pressure using a wall potential $U_w$ on the basis of a standard assumption\[^{11},^{12}\] concerning the relation between the force exerted by the wall $U_w$ on the various particles and a hydrostatic pressure $P$:

$$
\sum_i (\mathbf{r}_i \cdot \nabla_i U_w) = \oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S} = P \oint_{\partial V} \mathbf{r} \cdot d\mathbf{S} = 3PV. \quad (2.5)
$$

Furthermore, the thermodynamic pressure of this system is shown to be identical with the ‘kinetic’ pressure in the form:

$$
3PV = -3V \left[ \frac{\partial F}{\partial V} \right]_{TNU_{\text{ex}}(r)} = 2\langle \dot{T} \rangle - \sum_i (\mathbf{r}_i \cdot \nabla_i \dot{U}_p) \equiv \sum_i (\mathbf{r}_i \cdot \nabla_i U_w), \quad (2.6)
$$

where the potential operator $\dot{U}_p$ is interpreted as involving the external potential $U_{\text{ex}}$, and $\dot{T}$ is the kinetic operator.\[^{12}–^{15}\] Therefore, it is necessary from (2.5) that the pressure takes a constant value at every point of the surface $\partial V$ for the volume parameter $V$ to be a natural variable. A simple example of this inhomogeneous system is an atom confined in a spherical wall with a nucleus fixed at its center.

As the first step to treat an electron-nucleus mixture on the basis of (2.4) which afford to use the DF theory, let us consider a mixture of electrons and nuclei with the infinite nuclear mass, confined in a finite volume $V$ by wall potentials, $U_{\text{ele}}^w$ and $U_{\text{nuc}}^w$, respectively. Here, we assume this mixture constitutes a crystalline state in equilibrium, which is used as a model for the electron-band calculations. Since the nuclei remain at their fixed equilibrium positions, the nuclei make an external potential $U_{\text{ex}}(r)$ for the electrons, and the volume $V$ is a natural variable of this system. As a result, the pressure of this inhomogeneous electrons is determined by (2.4) in terms of the electron free energy $F_e$, which is explicitly defined later in (4.2).

It is important to notice that the derivatives must be performed under the external potential being fixed. Therefore, the nuclei producing the external potential $U_{\text{ex}}$ for the electrons do not contribute to the pressure; the pressure is the electron pressure in the similar meaning to that of a noninteracting electron gas under the external potential. Since the electron free energy $F_e$ can be described exactly in terms of the DF theory,\[^{10}\] the electron pressure $\hat{P}_e$ is shown (see Appendix A) to be

$$
\hat{P}_e = -\left. \frac{\partial F_e^{\text{DF}}}{\partial V} \right|_{TNU_{\text{ex}}(r)} = \left[ 2T_e + U_e - \sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \right] / 3V \quad (2.7)
$$

$$
= \left[ 2\langle \hat{T}_e \rangle_e - \sum_i (\mathbf{r}_i \cdot \nabla_i \hat{U}_e) \right] / 3V = \left[ \sum_i (\mathbf{r}_i \cdot \nabla_i U_{\text{ele}}^w) \right] / 3V, \quad (2.8)
$$

where the bracket with a suffix $e$ denotes the average over the electron states at a fixed nuclear configuration. Really, this can be also proven from (2.6) and (2.4). Therefore, the electron pressure given above is a thermodynamic quantity, that is,
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a physical quantity defined uniquely. Also, note that the electron pressure can be defined by a wall potential $U_{w}^{le}$. However, it should be kept in mind that this pressure is not defined as a quantity of the homogeneous mixture.

[i-b] In the second step to relate the above inhomogeneous system to a homogeneous electron-nucleus mixture, we consider this system to be a binary mixture of electrons and nuclei. Then, the total pressure of this homogeneous mixture is written as

$$3PV = 2\langle \hat{T}_{e} \rangle_{e} - \sum_{i} \langle \hat{r}_{i} \cdot \nabla_{i} \hat{U} \rangle_{e} - \sum_{\alpha} \langle \hat{R}_{\alpha} \cdot \nabla_{\alpha} \hat{U} \rangle_{e}$$

$$\equiv \sum_{i} \langle \hat{r}_{i} \cdot \nabla_{i} U_{w}^{rel} \rangle_{e} + \sum_{\alpha} \hat{R}_{\alpha} \cdot \nabla_{\alpha} U_{w}^{mc}$$

$$= 3P_{e}V + \sum_{\alpha} \hat{R}_{\alpha} \cdot F_{\alpha} = 2T_{e} + U_{e} = \sum_{i} \langle \hat{r}_{i} \cdot \nabla_{i} U_{w}^{rel} \rangle_{e} - \sum_{\alpha} \hat{R}_{\alpha} \cdot F_{\alpha}$$

(2.9)

since the nuclei have infinite mass and do not move, but stay at their equilibrium positions. Note that the pressure of this homogeneous mixture is described in terms of the electron pressure $P_{e}$ defined by (2.7) for the inhomogeneous system. Also, all of the nuclear forces $F_{\alpha}$ are zero except for nuclei near the surface in the short range of the wall potential, since the nuclei are in their equilibrium positions. On the other hand, the wall forces satisfying $F_{\alpha} = -F_{\alpha}$ near the surface describe the nuclear pressure. Thus, we can see that the total pressure is composed of the electron and nuclear pressures. In the derivation of (2.9), we have used the virial theorem for a homogeneous binary mixture confined in the volume $V$ by a wall, which produces potentials, $U_{w}^{A}$ and $U_{w}^{B}$, for A and B particles, respectively;

$$3PV = -3V \frac{\partial F_{e}}{\partial V} \bigg|_{TN} = 2\langle \hat{T}_{A} \rangle - \sum_{i} \langle \hat{r}_{i} \cdot \nabla_{i} \hat{U}_{p} \rangle + 2\langle \hat{T}_{B} \rangle - \sum_{\alpha} \langle \hat{R}_{\alpha} \cdot \nabla_{\alpha} \hat{U}_{p} \rangle$$

$$\equiv \sum_{i} \langle \hat{r}_{i} \cdot \nabla_{i} U_{w}^{A} \rangle + \sum_{\alpha} \langle \hat{R}_{\alpha} \cdot \nabla_{\alpha} U_{w}^{B} \rangle. \quad (2.10)$$

[ii] Furthermore, when the nucleus has a finite mass, but behaves as a classical particle which makes the relations in the adiabatic approximation exact, the electron pressure of an homogeneous electron-nucleus mixture is given by the configuration average over $\{R_{\alpha}\}$ of the electron pressure in the inhomogeneous electrons under the external potential $U_{ex}(r|\{R_{\alpha}\})$:

$$3P_{e}V = \left. -3V \frac{\partial F_{e}}{\partial V} \right|_{TN, U_{ex}(r)} = 2\langle \hat{T}_{e} \rangle - \sum_{i} \langle \hat{r}_{i} \cdot \nabla_{i} \hat{U} \rangle$$

(2.11)

as will be discussed later in [ii]. [iii] Even when the nuclei behave as quantum particles, Eq. (2.11) is valid in the adiabatic approximation.10 Therefore, this virial theorem (2.10) suggests that we can define the electron pressure in a general form even when the adiabatic approximation becomes invalid, as is described in the following.
From the Hamiltonian (2.1), we can obtain the following relation:
\[ \langle \Psi_m | \hat{r}_i \cdot \hat{p}_i, \hat{H} | \Psi_m \rangle = i\hbar \langle \Psi_m | \{ \hat{p}_i^2 / m - \hat{r}_i \cdot \nabla_i \hat{U} \} | \Psi_m \rangle = 0 , \] (2.12)
due to the Hermitian property of the operator \( \hat{r}_i \cdot \hat{p}_i \) of \( i \)-electron. Here, \( \Psi_m \) denotes an eigenfunction of the Hamiltonian \( \hat{H} \). The ensemble average of the electron kinetic energy is related to the interacting potential by use of (2.12)
\[ 2 \langle \hat{p}_i^2 / 2m \rangle = \langle \hat{r}_i \cdot \nabla_i \hat{U} \rangle . \] (2.13)
In addition, we obtain the similar relation for a nucleus in the system
\[ 2 \langle \hat{P}_\alpha^2 / 2M \rangle = \langle \hat{R}_\alpha \cdot \nabla_\alpha \hat{U} \rangle . \] (2.14)
Here, the ensemble average of an operator \( A \) is defined by
\[ \langle A \rangle \equiv \text{Tr}[\exp(-\beta \hat{H})A]/\text{Tr}[\exp(-\beta \hat{H})] , \] (2.15)
where the trace is taken over a complete set of states of the electron-nucleus mixture.

Therefore, when the electrons and the nuclei are confined in a volume \( V \) by a wall with wall potentials, \( U_{\text{ele}}^w \) and \( U_{\text{nuc}}^w \), respectively, Eqs. (2.13) and (2.14) for this system are written in the following forms relating the electron and nuclear kinetic energies, \( \hat{T}_e \) and \( \hat{T}_N \), respectively:
\[ 2 \langle \hat{T}_e \rangle = \sum_i \langle \hat{r}_i \cdot \nabla_i \hat{U} \rangle + \sum_i \langle \hat{r}_i \cdot \nabla_i U_{\text{ele}}^w \rangle \] (2.16)
\[ 2 \langle \hat{T}_N \rangle = \sum_\alpha \langle \hat{R}_\alpha \cdot \nabla_\alpha \hat{U} \rangle + \sum_\alpha \langle \hat{R}_\alpha \cdot \nabla_\alpha U_{\text{nuc}}^w \rangle , \] (2.17)
where the wall potentials should be taken into account in the ensemble average (2.15) by adding them to the Hamiltonian\(^{16,17}\) or as the boundary condition\(^{12-15}\) to solve the wave equation. At this point, it should be kept in mind that the interactions of the particles with the wall can be omitted from the new Hamiltonian if the boundary condition that \( \Psi = 0 \) for any particle on the wall is made.\(^{12,14,15}\) As a result, with use of the Hamiltonian (2.1) and this boundary condition, the electron and nuclear pressures are expressed respectively in the forms:
\[ 3P_e V \equiv \sum_i \langle \hat{r}_i \cdot \nabla_i U_{\text{ele}}^w \rangle = -\sum_i \langle \hat{r}_i \cdot \hat{F}_i^w \rangle = 2\langle \hat{T}_e \rangle - \sum_i \langle \hat{r}_i \cdot \nabla_i \hat{U} \rangle = 2\langle \hat{T}_e \rangle + \langle \hat{U} \rangle - \sum_\alpha \langle \hat{R}_\alpha \cdot \hat{F}_\alpha \rangle \] (2.18)
\[ 3P_N V \equiv \sum_\alpha \langle \hat{R}_\alpha \cdot \nabla_\alpha U_{\text{nuc}}^w \rangle = -\sum_\alpha \langle \hat{R}_\alpha \cdot \hat{F}_\alpha^w \rangle = 2\langle \hat{T}_N \rangle - \sum_\alpha \langle \hat{R}_\alpha \cdot \nabla_\alpha \hat{U} \rangle , \] (2.19)
since the external virials, \( \sum_i \langle \hat{r}_i \cdot \nabla_i U_{\text{ele}}^w \rangle \) and \( \sum_\alpha \langle \hat{R}_\alpha \cdot \nabla_\alpha U_{\text{nuc}}^w \rangle \), enable us to define the electron and nuclear pressures, respectively, on the base of the standard assumption:
$\sum_i (\hat{r}_i \cdot \nabla_i U_w) = f_{\partial V} \cdot dS$.\textsuperscript{11,12,15}) For the volume parameter $V$ to be a natural variable, the pressures, $P_e$ and $P_N$, must take a constant value at every point of the surface $\partial V$. In the above, Eq. \textsuperscript{(2.19)} is derived by the relation \textsuperscript{(2.3)}, and the force on $\alpha$-nucleus is given by $\hat{F}_\alpha = -\nabla_\alpha \hat{U}$. The definition of the electron pressure \textsuperscript{(2.18)} can be used even when the nuclei behave as quantum particles \textit{without use of any approximation}.

At this stage, we can construct the following three systems of electron-nucleus mixtures by choosing the electron and nuclear wall potentials in different ways.

(I) System-I, where the electrons and nuclei are confined in the volume $V$. In this system, the total pressure is given by

$$3PV = 3(P_e + P_N)V = 2\langle \hat{T}_e \rangle + 2\langle \hat{T}_N \rangle + \langle \hat{U} \rangle \equiv 3P_I V.$$  \hspace{1cm} (2.22)

(II) System-II, where $U^{\text{ele}}_w = 0$ and $U^{\text{nuc}}_w \neq 0$. In this system, the electron pressure becomes zero because of \textsuperscript{(2.18)}:

$$3P_e V_e = 0 = 2\langle \hat{T}_e \rangle + \langle \hat{U} \rangle - \sum_\alpha \langle \hat{R}_\alpha \cdot \hat{F}_\alpha \rangle.$$  \hspace{1cm} (2.23)

Therefore, the total pressure of this system can be attributed only to the nuclear part:

$$3PV = 2\langle \hat{T}_N \rangle - \sum_\alpha \langle \hat{R}_\alpha \cdot \nabla_\alpha \hat{U} \rangle = 2\langle \hat{T}_N \rangle + \sum_\alpha \langle \hat{R}_\alpha \cdot \hat{F}_\alpha \rangle$$  \hspace{1cm} (2.24)

$$= 2\langle \hat{T}_N \rangle + 2\langle \hat{T}_e \rangle + \langle \hat{U} \rangle \equiv 3P_{II} V,$$  \hspace{1cm} (2.25)

At this point, it should be noted that the zero pressure relation \textsuperscript{(2.23)} is used in the derivation of \textsuperscript{(2.25)} from \textsuperscript{(2.24)}.

(III) System-III, where $U^{\text{nuc}}_w = 0$ and $U^{\text{ele}}_w = 0$. This system represents nothing but an electron-nucleus mixture in the vacuum, where $P_e = 0$ and $P_N = 0$ due to \textsuperscript{(2.18)} and \textsuperscript{(2.20)}. Consequently, the total pressure of this system becomes zero: $P = P_e + P_N = 0$.

On the basis of the fundamental relations derived here in conjunction with System-I, II and III constructed in the above, we can make the following statements from (A) to (E):

(A) : The electron pressure $P_e$ and the nuclear pressure $P_N$ can be clearly defined for an electron-nucleus mixture by \textsuperscript{(2.19)} and \textsuperscript{(2.21)}, respectively; the total pressure is a sum of the electron and nuclear pressures, as shown in \textsuperscript{(2.22)}.

(B) : The electron pressure is described by \textsuperscript{(2.19)}, where the nuclear virial is subtracted.

(C) : The pressure of System-I is the thermodynamic pressure of an electron-nucleus mixture. It has been shown that the pressure defined by the sum of \textsuperscript{(2.19)} and \textsuperscript{(2.21)} becomes identical with the thermodynamic pressure determined by the volume derivative of free energy.\textsuperscript{12–17}

(D) : The pressure $P_I$ in System-I has an identical expression to $P_{II}$ in System-II. Therefore, some investigators\textsuperscript{1,2,4} believe that System-II is identical to
System-I in the sense that both systems provide the same thermodynamic quantities (e.g., the pressure). However, the pressures, $P_I$ and $P_{II}$, are equal with each other only when these systems are nearly equal to the system-III ($P_e = P_N = 0$). It should be noticed that System-II is in general an inhomogeneous system, since this model involves a superatom in the extreme limit ($V \to 0$) with all nuclei compressed to become a point charge as this mathematical model. On the other hand, System-I is always homogeneous, since the wall effect can be replaced by periodic boundary conditions for this system. Therefore, System-I and System-II are different from each other in general, although (2.22) and (2.25) have the identical expression; a physical quantity $P_e$ is not zero in the one and zero, in the other as Eq. (2.23) indicates.

(E) : A metal in the vacuum is defined as an electron-nucleus mixture without the wall potentials to confine the electrons ($U_{ew}^{ele} = 0$) and the nuclei ($U_{ew}^{nuc} = 0$) in a finite volume. Therefore, by definition the thermodynamic pressure of a metal in the vacuum is zero, which is realized by the condition $P_e = 0$ and $P_N = 0$, as System-III exhibits: this results from the virial theorem for single particle, (2.13) and (2.14). This fact makes a contrast to the usual treatment of a metal where the pressure of a metal becomes zero as a result of the cancellation in a sum: $P = P_e + P_N = 0$ with $P_e < 0$ and $P_N > 0$.\(^{5,6}\)

\section*{§3. Electron and nuclear stress tensors}

In the present section, we derive formulae of stress tensors by the same arguments that were advanced in the preceding section treating the pressure in an electron-nucleus mixture. In the electron-nucleus mixture where the electrons and nuclei are confined in the same volume $V$ (System-I), Nielsen and Martin [NM]\(^{18}\) proved that the stress intrinsic to the system is given by a sum of the electron and nuclear parts:

$$T_{\mu\nu} = T_{\mu\nu}^{ele} + T_{\mu\nu}^{nuc}$$  \hspace{1cm} (3.1)

with the definitions of the electron and nuclear stress tensors by

$$T_{\mu\nu}^{ele} = -\sum_i \left\langle \hat{P}_{\mu} \hat{P}_{\nu} m \right. - \hat{r}_{i\mu} \nabla_{i\nu} \hat{U} \right\rangle$$  \hspace{1cm} (3.2)

$$T_{\mu\nu}^{nuc} = -\sum_\ell \left\langle \frac{\hat{P}_{\ell\mu} \hat{P}_{\ell\nu}}{M} - \hat{R}_{\ell\mu} \nabla_{\ell\nu} \hat{U} \right\rangle = -Nk_B T \delta_{\mu\nu} - \sum_\ell \left\langle \hat{R}_{\ell\mu} \hat{F}_{\ell\nu} \right\rangle,$$  \hspace{1cm} (3.3)

respectively. In the framework of the DF theory, the electron stress tensor is written in the form:

$$T_{\mu\nu}^{ele} = -\sum_k \left\langle f(\epsilon_k) \left( \frac{\hat{P}_{\mu} \hat{P}_{\nu}}{m} - \phi_k \right) \phi_k \right\rangle_N - \frac{1}{2} \int \left\langle \rho(\mathbf{r}) \rho(\mathbf{r}') \right\rangle_N \frac{(\mathbf{r} - \mathbf{r}')_\mu (\mathbf{r} - \mathbf{r}')_\nu}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r} d\mathbf{r}'$$

$$+ \int \left\langle \sigma^{xc}_{\mu\nu} \right\rangle_N d\mathbf{r} + \sum_\ell \left\langle \hat{R}_{\ell\mu} \hat{F}_{\ell\nu} \right\rangle_N,$$  \hspace{1cm} (3.4)
where the bracket with N suffix indicates the configurational average of $A(\{R_\alpha\})$ defined by

$$\langle A \rangle_N \equiv \frac{1}{\Xi} \int dR^N \exp(-\beta F_e[n; \{R_\alpha\}]) A(\{R_\alpha\}) \tag{3.5}$$

with

$$\Xi \equiv \int dR^N \exp(-\beta F_e[n; \{R_\alpha\}]).$$

Here, the exchange-correlation stress tensor $\sigma^{xc}$ is defined in the DF theory as

$$\nabla \cdot \sigma^{xc} \equiv -n(r) \nabla \frac{\delta F_{xc}}{\delta n(r)}, \tag{3.6}$$

in terms of the exchange-correlation part $F_{xc}$ of the free-energy for electrons in the fixed nuclei, and $f(\epsilon_k)$ denotes the occupation probability for a state $\epsilon_k$ determined by the Kohn-Sham equation with its wave function $\phi_k$. Also, the electrostatic energy $E_{es}[n]$ of the nucleus-electron mixture is written as

$$E_{es}[n] \equiv \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} d\mathbf{r} d\mathbf{r}' - \sum_{\ell=1}^N \int \frac{Ze^2 n(r')}{|r'-R_\ell|} d\mathbf{r}' + \frac{1}{2} \sum_{\alpha\beta} \frac{Z^2 e^2}{|R_\alpha - R_\beta|} \tag{3.7}$$

$$\equiv E_{ee} + E_{en} + E_{nn} = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d\mathbf{r} d\mathbf{r}' = E_{es}[n, \tilde{n}] \tag{3.8}$$

with $\rho(r) \equiv -en(r) + Ze\tilde{n}(r)$ and $\tilde{n}(r) \equiv \sum_\ell \delta(r - R_\ell)$. In the derivation of (3.3), we have used the relation:

$$\frac{1}{2} \int \rho(r)\rho(r') \frac{(r-r')_\mu(r-r')_\nu}{|r-r'|^3} d\mathbf{r} d\mathbf{r}' = -\int n(r)r_\mu \nabla_\nu \frac{\delta E_{es}}{\delta n(r)} d\mathbf{r} - \sum_\ell R_{\ell\mu} \nabla_\nu E_{es}. \tag{3.9}$$

Therefore, by the combined use of (3.3) and (3.4), the total stress tensor $T_{\mu\nu}$ is represented as

$$T_{\mu\nu} = -Nk_B T_{\delta_{\mu\nu}} - \sum_{k} \left\langle f(\epsilon_k) \left( \phi_k \mid \frac{\hat{p}_\mu \hat{p}_\nu}{m} \mid \phi_k \right) \right\rangle_N$$

$$- \frac{1}{2} \int (\rho(r)\rho(r'))_N \frac{(r-r')_\mu(r-r')_\nu}{|r-r'|^3} d\mathbf{r} d\mathbf{r}' + \int (\sigma_{\mu\nu}^{xc})_N d\mathbf{r}, \tag{3.10}$$

which is essentially identical with the expression of the stress tensor given by NM if the nuclear kinetic term is neglected.

On the other hand, in the system where only the nuclei are confined in the volume $V$ (System II), the total stress tensor is given by

$$T_{\mu\nu} = T_{\mu\nu}^{nuc} = -Nk_B T_{\delta_{\mu\nu}} - \sum_\ell \langle R_{\ell\mu} F_{\ell\nu} \rangle_N \tag{3.11}$$

which leads to the identical expression to (3.10), since the electron stress tensor $T_{\mu\nu}^{ele}$ becomes zero in this system. On the basis of System-II with the infinite nuclear
mass, Ziesche et al.⁴) and Dal Corso and Resta¹⁹) have proposed to define the stress tensor in terms of the nuclear forces. In fact, Dal Corso and Resta have used the relation $T^{\text{ele}}_{\mu\nu} = 0$ in their derivation of (3.10) from (3.11). In spite of (3.11) leading to the same expression to (3.10), these formulae yield different results with each other for each system, since System-I is a homogeneous system while System-II is an inhomogeneous system in general. In a metallic system under high pressure, the electron stress tensor $T^{\text{ele}}_{\mu\nu}$ plays an important role compared with the nuclear stress tensor $T^{\text{nuc}}_{\mu\nu}$.

§4. Definitions of electron pressure

As mentioned in §2, the virial theorem shows that the total pressure of an electron-nucleus mixture is given by a sum of the nuclear and electron pressures; the concept of the electron pressure is clearly defined by using the wall potential $U^w_{\text{ele}}$ for the electrons in the form of (2.19), which is applicable to this mixture without use of the adiabatic approximation. On the other hand, many types of definitions for the electron pressure have been proposed up to date within the adiabatic approximation. At the first, the thermodynamic electron pressure is defined on the basis of the thermodynamic relation

(I)  \[ \tilde{P}_e \equiv -\frac{\partial F_e}{\partial V} \bigg|_{TN_e\{R_\alpha\}} \],

by introducing the electron free-energy $F_e[n; \{R_\alpha\}]$ for the electrons in the electron-nucleus mixture confined in the volume $V$: the nuclei are assumed as classical particles, which produce an external potential for electrons in the system. This free energy, $F_e[n; \{R_\alpha\}]$, is defined by the electron part of the Hamiltonian for this mixture in the form

\[ F_e[n; \{R_\alpha\}] \equiv -k_B T \ln \operatorname{Tr}_e \exp[-\beta (\hat{T}_e + \hat{U})], \]

where $\operatorname{Tr}_e$ is the trace operator which is taken over a complete set of states of the electrons in the system; (4.2) is the free energy of the electrons under the external potential caused by the nuclei fixed at $\{R_\alpha\}$. The DF theory provides an exact expression for the free energy of the electrons in this system in the form

\[ F^{\text{DF}}_e[n; \{R_\alpha\}] \equiv F_0 + E_{\text{es}}[n, \tilde{n}_I] + F_{\text{xc}}[n, \tilde{n}_I] \]  \[ (4.3) \]

with use of $F_0$, the free energy of a noninteracting electron gas, and the exchange-correlation contribution $F_{\text{xc}}$ to the free energy.

In contrast to the above macroscopic definitions of the electron pressure, we can define the pressure in a microscopic way. In this spirit, Bader²¹)–²³) introduced the microscopic electron pressure tensor $\tilde{P}_e$ by treating an electron-gas in the fixed nuclei as an interacting many-body system in the form:

(II)  \[ \nabla \cdot \tilde{P}_e \equiv \mathbf{F}(r), \]

where the force density $\mathbf{F}(r)$ is defined by use of the binary correlation function...
\( \Gamma^{(2)}(\mathbf{r}, \mathbf{r}') \) as
\[
\mathbf{F}(\mathbf{r}) = n(\mathbf{r}) \sum_\alpha \nabla \frac{Z e^2}{|\mathbf{r} - \mathbf{R}_\alpha|} - 2 \int d\mathbf{r}' \nabla \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \Gamma^{(2)}(\mathbf{r}, \mathbf{r}').
\] (4.5)

In a similar way, More\(^{24,25}\) defined the electron pressure tensor based on the fact that the electron gas is in hydrostatic equilibrium at each point in the electron-nucleus mixture with the pressure variations by electrical forces as is written in the following form:
\[
\nabla \cdot \mathbf{\tilde{P}}_e \equiv -n(\mathbf{r}) \nabla \left[ -\sum_{\alpha=1}^N \frac{Z e^2}{|\mathbf{r} - \mathbf{R}_\alpha|} + \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] = -n(\mathbf{r}) \nabla \frac{\delta E_{es}}{\delta n(\mathbf{r})}. \tag{4.6}
\]
The same definition was introduced by Bartolotti and Parr\(^{26}\) from a more general point of view. On the basis of the DF theory, the microscopic electron pressure tensor \( \mathbf{\tilde{P}}_e \) defined by (4.6) is shown to be written explicitly by the sum of the electron kinetic tensor \( \mathbf{P}_{DF}^K \) and the exchange-correlation pressure tensor \( \mathbf{P}_{DF}^{xc} \):
\[
\mathbf{\tilde{P}}_e \equiv \mathbf{P}_{DF}^K + \mathbf{P}_{DF}^{xc},
\] (4.7)
where \( \mathbf{P}_{DF}^K \) is defined in terms of the wave functions \( \phi_i \) for the Kohn-Sham equation as
\[
\mathbf{P}_{DF}^K \equiv \sum_i f(\epsilon_i) \frac{-\hbar^2}{4m} \left[ \phi_i \nabla_\mu \nabla_\nu \phi_i^* + \phi_i^* \nabla_\mu \nabla_\nu \phi_i - \nabla_\mu \phi_i \nabla_\nu \phi_i^* - \nabla_\mu \phi_i^* \nabla_\nu \phi_i \right], \tag{4.8}
\]
and the exchange-correlation contribution \( \mathbf{P}_{DF}^{xc} \) is defined in the DF theory as
\[
\nabla \cdot \mathbf{P}_{DF}^{xc} \equiv n(\mathbf{r}) \nabla \frac{\delta F_{xc}}{\delta n(\mathbf{r})}. \tag{4.9}
\]
In this definition, the thermodynamic pressure is given by the following surface integral over the surface of the system:
\[
3\mathbf{\tilde{P}}_e V = \oint_{\partial V} \mathbf{r} \cdot \mathbf{\tilde{P}}_e \cdot d\mathbf{S}. \tag{4.10}
\]
which can be transformed in the volume-integral form:\(^{27}\)
\[
3\mathbf{\tilde{P}}_e V = 2T_s + E_{es} + \int_V \text{tr} \mathbf{P}_{DF}^{xc} d\mathbf{r} - \sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha, \tag{4.11}
\]
in terms of the kinetic-energy functional \( T_s \), where the operator \( \text{tr} \) means to take the sum of the diagonal terms of tensor. In the same scheme, another form of microscopic electron pressure tensor was introduced by Nielsen, Martin, Ziesche,\(^3,18\) and Folland\(^{28}\) with use of the Maxwell pressure tensor \( \mathbf{P}_M \):
\[
\mathbf{\tilde{P}}_e \equiv \mathbf{P}_{DF}^K + \mathbf{P}_{DF}^{xc} + \mathbf{P}_M. \tag{4.12}
\]
On the other hand, the electron pressure is determined by the formula based on the force theorem,\(^{10,29,30}\)

\[
3 \tilde{P}_e V = -3 V \sum_i f(\epsilon_i) \frac{d \epsilon_i}{dV} |_{U_{\text{self}}} + \oint_{\partial V} \mathbf{r} \cdot \mathbf{P}_{\text{DF}}^{\text{xc}} \cdot d\mathbf{S},
\]

(4.13)

where the volume derivative of the Kohn-Sham eigenvalue \(\epsilon_i\) is performed under the self-consistent potential \(U_{\text{self}}\) being fixed. From a different point of view from the above pressure definitions, Janak\(^1\) and Ziesche \textit{et al.}\(^4\) made a definition of the electron pressure with use of the total force on the nuclei in the form

\[
3 \tilde{P}_e V = \sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha.
\]

(VI) \hspace{1cm} (4.14)

In spite of different expressions, it can be shown that all definitions of the electron pressure, (I)-(V), except (VI), lead to the same pressure formula for the electrons confined in the volume \(V\) (see also Appendix A) as follows:\(^{21,29,27,10}\)

\[
3 \tilde{P}_e V = 2 \langle \hat{T}_e \rangle_e + \langle \hat{U} \rangle_e - \sum_\alpha \langle \hat{R}_\alpha \cdot \hat{F}_\alpha \rangle_e = \oint_{\partial V} \mathbf{r} \cdot \mathbf{\tilde{P}}_e \cdot d\mathbf{S}.
\]

(4.15)

It should be noticed that the pressure defined by (4.12) with use of the Maxwell pressure tensor can play the role of the electron pressure only under the condition that the relation, \(\oint_{\partial V} \mathbf{r} \cdot \mathbf{P}_{\text{M}} \cdot d\mathbf{S} = 0\), is fulfilled on the surface \(\partial V\) of the volume \(V\). In fact, many investigators\(^{31-33,30}\) use a surface-integral expression (4.15) for calculating the electron pressure in solids. On the other hand, the definition (VI) leads to the relation \(^1\), \(^4\)

\[
3 \tilde{P}_e V = \sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha = \sum_\alpha \langle \hat{R}_\alpha \cdot \hat{F}_\alpha \rangle_e = 2 \langle \hat{T}_e \rangle_e + \langle \hat{U} \rangle_e,
\]

(4.16)

with use of the adiabatic approximation and the Hellmann-Feynman theorem. Although the right-hand side of (4.16) has an appropriate form of the virial theorem consisting of two times of the electron kinetic energy and the potential energy, Eq. (4.16) cannot be taken as providing the electron pressure; this equation itself means \(P_e = 0\) because of (2.19) in Sec. 2. It is rather appropriate to consider that the pressure defined by (4.14) provides the total pressure for another inhomogeneous system (System-II), that is, the electron-nucleus mixture where only the nuclei are confined in the volume \(V\) in the case where the nuclear kinetic pressure can be neglected (see also Appendix B). In some works,\(^{34,35}\) the electron pressure is defined by the variation of the electron internal energy per unit cell with respect to the cell volume \(\Omega\) under the fixed entropy \(S\) and total electron number \(N_e\):

\[
\hat{P}_e \equiv - \frac{\partial E_e^\Omega}{\partial \Omega} |_{S,N_e}.
\]

(VII) \hspace{1cm} (4.17)

This definition also leads to the relation \(3 \tilde{P}_e V = 2 \langle \hat{T}_e \rangle + \langle \hat{U} \rangle\), since the nuclear coordinates are not fixed in the \(\Omega\)-derivative of this definition (see Appendix A). Note
Electron and nuclear pressures

that the pressure (4.17) is not the electron pressure, but provides the total pressure for an electron-nucleus mixture where the nuclear mass is taken to be infinite, as is shown in (2.3).

At this point, it is important to notice that the microscopic pressure tensor \( \hat{P}_e^M \) defined by (4.12) can provide a pressure formula for an arbitrary subspace with a volume \( \Omega \) in the system as follows:

\[
3 \hat{P}_e \Omega = \int_{\partial \Omega} \mathbf{r} \cdot \hat{P}_e^M \cdot d\mathbf{S} = \int_{\Omega} \text{tr} \hat{P}_e^M d\mathbf{r} - \sum_{\alpha \in \Omega} \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha = \int_{\partial \Omega} \mathbf{r} \cdot \hat{P}_e \cdot d\mathbf{S} \tag{4.18}
\]

\[
= 2T_s [n]_{\Omega} + E_{es}(\Omega) + \int_{\Omega} \text{tr} P_{xc} d\mathbf{r} - \sum_{\alpha \in \Omega} \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha , \tag{4.19}
\]

if \( \hat{P}_e^M \) is constant on the surface \( \partial \Omega \) of a volume \( \Omega \) and \( \oint_{\partial \Omega} \mathbf{r} \cdot \mathbf{P}_e^M \cdot d\mathbf{S} = 0 \). Here, the electrostatic energy \( E_{es}(\Omega) \) contained in the subspace \( \Omega \) is defined as

\[
E_{es}(\Omega) \equiv - \int_{\Omega} \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \phi(\mathbf{r}) d\mathbf{r} \tag{4.20}
\]

\[
= \frac{1}{8\pi} \int_{\Omega} |\mathbf{E}|^2 d\mathbf{r} - \oint_{\partial \Omega} \mathbf{r} \cdot \mathbf{P}_e^M \cdot d\mathbf{S} \tag{4.21}
\]

with use of the electric field \( \mathbf{E} = -\nabla \phi \) and the electric potential

\[
e\phi(\mathbf{r}) \equiv \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \sum_{\alpha=1}^{N} \frac{Ze^2}{|\mathbf{r} - \mathbf{R}_\alpha|} = \frac{\delta E_{es}}{\delta n(\mathbf{r})} . \tag{4.22}
\]

In the above, it is important to recognize that the electrostatic energy \( E_{es}(\Omega) \) contained in a subspace \( \Omega \) is not always equal to \( \int_{\Omega} |\mathbf{E}|^2 d\mathbf{r}/8\pi \), as was defined in some works.\(^{24}\) Also, the kinetic energy \( T_s [n]_{\Omega} \) involved in the volume \( \Omega \) is written from (4.8) as

\[
2T_s [n]_{\Omega} \equiv \int_{\Omega} \text{tr} P_{DF} d\mathbf{r} \tag{4.23}
\]

\[
= \sum_{i} f(\epsilon_i) \int_{\Omega} \left[ \phi_i \frac{-\hbar^2}{2m} \nabla^2 \phi_i + \frac{1}{2m} \left| \frac{\hbar}{i} \nabla \phi_i \right|^2 \right] d\mathbf{r} \tag{4.24}
\]

\[
= 2 \sum_{i} f(\epsilon_i) \int_{\Omega} \phi_i \frac{-\hbar^2}{2m} \nabla^2 \phi_i d\mathbf{r} + \frac{\hbar^2}{4m} \int_{\Omega} \nabla^2 n(\mathbf{r}) d\mathbf{r} . \tag{4.25}
\]

In a similar way with use of the Maxwell pressure tensor, the electron part of the stress tensor is given for a subspace \( \Omega \) of the system by the formula

\[
\hat{T}^{ele}_{\Omega} = - \int_{\Omega} \hat{P}_e^M d\mathbf{r} + \sum_{\ell \in \Omega} \mathbf{R}_\ell \circ \mathbf{F}_\ell = - \oint_{\partial \Omega} \mathbf{r} \circ \hat{P}_e^M \cdot d\mathbf{S} = - \oint_{\partial \Omega} \mathbf{r} \circ \hat{P}_e \cdot d\mathbf{S} , \tag{4.26}
\]

with the symbol \( \circ \) denoting a dyadic product of two vectors.
§5. Equation of states for liquid metals

In §2, we have proven that the pressure of an electron-nucleus mixture is expressed by a sum of the electron and nuclear pressures, which are clearly defined in the virial forms. In the present section, we derive a virial pressure formula for simple liquid metals based on this fact, and the zero pressure condition is examined numerically for this pressure formula.

5.1. Derivation of a virial pressure formula

The standard virial pressure formula for a simple metal as an electron-ion mixture is written in a complicated form to calculate owing to the volume derivative of the effective ion-ion interaction in the formula.\(^{36}\) In contrast to this standard expression, the virial theorem described in §2 provides the equation of states (EOS) in a simple form:

\[
3PV = 3(P_e + P_N)V \equiv 2\langle \hat{\mathbf{T}}_e \rangle - \sum_i \langle \hat{\mathbf{r}}_i \cdot \nabla_i \hat{U} \rangle - \sum_{\alpha} \langle \hat{\mathbf{R}}_{\alpha} \cdot \nabla_{\alpha} \hat{U} \rangle (5.1)
\]

\[
= 3P_e V + 3Nk_B T + \sum_{\alpha} \langle \mathbf{R}_{\alpha} \cdot \mathbf{F}_{\alpha} \rangle _N, (5.2)
\]

by regarding liquid metals as a mixture of electrons and nuclei. In a simple liquid metal, the interaction among ions with the Coulomb potential \(v_{\text{II}}^{\text{eff}}(Q)\) can be approximated as a sum of binary interaction \(v_{\text{eff}}(r)\), which is defined in the quantum hypernetted chain (QHNC) theory\(^{37}\) by

\[
\beta v_{\text{II}}^{\text{eff}}(Q) \equiv \beta v_{\text{II}}^{c}(Q) - \frac{|C_{\text{el}}(Q)|^2 n_{0}^{e} \chi_{Q}^{0}}{1 + \beta n_{0}^{e} v_{\text{ee}}^{c}(Q)[1 - G(Q)]\chi_{Q}^{0}}. (5.3)
\]

Here, \(C_{\text{el}}(Q)\) denotes the electron-ion direct correlation function, which plays the role of a pseudopotential \(w(Q) = -C_{\text{el}}(Q)/\beta\), and \(\chi_{Q}^{0}\), the density-density response function of a noninteracting electron gas, with \(G(Q)\) being the local-field correction. Therefore, with use of this two-body interaction, the EOS is written as follows:

\[
3PV = 3P_e V + 3Nk_B T - N\frac{1}{2} n_{0}^{e} \int g_{\text{II}}(r) r \nabla v_{\text{eff}}^{c}(r) d\mathbf{r}. (5.4)
\]

At the next step, we proceed to derive an approximate representation of the electron pressure \(P_e\) in (5.4) on the basis of the spherical cell model. By taking a Wigner-Seitz sphere with a radius \(R\), the electron pressure can be represented by the surface integral over the surface \(S\) in the form:\(^{27}\)

\[
P_e = \frac{1}{3\Omega} \int_{S} \mathbf{r} \cdot (\mathbf{P}^{\text{DF}}_{\text{R}} + \mathbf{P}^{\text{DF}}_{\text{xc}}) \cdot d\mathbf{S} = P_k(R) + P_{\text{xc}}(R). (5.5)
\]

In the above, the kinetic pressure \(P_k(R)\) is given in units of hartree in the form:\(^{33}\)

\[
P_k(R) = \frac{1}{8\pi} \sum_{k\ell} f(\epsilon_{k\ell} - \bar{\mu}) |\phi_{k\ell}(R)|^2 \left[ \frac{(D_{k\ell} - \ell)(D_{k\ell} + \ell + 1)}{R^2} + 2\{\epsilon_{k\ell} - V_{\text{eff}}(R)\} \right], (5.6)
\]
with
\[ D_{k\ell} \equiv R \frac{1}{\phi_{k\ell}} \left. \frac{d\phi_{k\ell}}{dr} \right|_R, \] (5.7)
and \( \bar{\mu} \) being the chemical potential. In the above, \( \phi_{k\ell}(r) \) denotes the radial part of the wave function for a state \( \epsilon_{k\ell} \) of angular momentum \( \ell \) satisfying
\[ \frac{d^2(r\phi_{k\ell})}{dr^2} + \left[ 2(\epsilon_{k\ell} - V_{\text{eff}}) - \frac{\ell(\ell + 1)}{r^2} \right] (r\phi_{k\ell}) = 0. \] (5.8)

In the SJ model, the whole crystal with dipole layer \( D \) at its surface is considered as an assembly of Wigner-Seitz cells with dipole-layer surface. As a result, by taking the zero of a potential to be at the vacuum level, the effective potential \( V_{\text{eff}} \) in the Wigner-Seitz sphere is written as
\[ V_{\text{eff}}(r) = v_{\text{en}} + \int v_{\text{ee}}(r-r') n(r')dr' + \mu_{\text{xc}}(r) - D\theta(R-r) \] (5.9)
with \( \theta(x) \) being the step function and \( \mu_{\text{xc}}(r) \equiv \delta F_{\text{xc}}/\delta n(r) \). With a choice of the zero of the potential to be \( V_{\text{eff}}(R^-) \), the electron pressure at the surface \( S \) takes a form:
\[ P_k(R) = -Dn(R) + \frac{1}{24\Omega\pi} \sum_{k\ell} f(\epsilon_{0k\ell} - \epsilon_F) |\phi_{k\ell}(R)|^2 \left[ \frac{(D_{k\ell} - \ell)(D_{k\ell} + \ell + 1)}{R^2} + 2\epsilon_{0k\ell} \right]. \] (5.10)

In the above, \( \epsilon_{0k\ell} \) and \( \epsilon_F \) indicate an energy level and Fermi energy with respect to this new origin, respectively, and the pressure at the surface is defined as \( P_k(R) \equiv P_k(R^+) \).

When the wave functions of electrons become plane waves and produce a constant density \( n \) near the boundary of the Wigner-Seitz sphere, the above equation leads to an approximate expression for the electron pressure as follows:
\[ P_e(n) = -Dn + n^2 \frac{d\epsilon_I}{dn}, \] (5.11)
in terms of the energy \( \epsilon_I \) per one electron in the jellium model.

Table I. The nuclear pressures (GPa) for alkaline liquid metals in the vacuum calculated by the QHNC method and the Ashcroft model potential (Rb). The nuclear kinetic and virial pressures are also shown together with the electron pressure given by \( P_e = n^2 \frac{d\epsilon_J}{dn} \big|_{n_0} \) (the jellium model). The nuclear pressures calculated by Kumaravadivel deviate significantly from the zero pressure condition compared with the QHNC results.

| Metal | \( n_0 k_B T \) | \( n_1 k_B T \) | nuclear virial | \( P_N \) | \( P_N^{44} \) | \( n^2 \frac{d\epsilon_J}{dn} \big|_{n_0} \) |
|-------|----------------|----------------|----------------|-------|-------------|----------------|
| Li    | 3.308          | 0.2888         | -0.2871        | 0.0017| -1.7        | 2.70           |
| Na    | 4.046          | 0.1253         | 0.0362         | 0.1615| -0.24       | 0.024          |
| Rb    | 5.388          | 0.0445         | 0.0734         | 0.1179| -0.89       | -0.34          |
In the jellium model, the electron pressure does not satisfy the condition $P_e = 0$ at equilibrium density $n_0$ in the vacuum. In contrast to this model the condition $P_e = 0$ at equilibrium density $n_0$ is fulfilled in the stabilized jellium (SJ) model\(^7,9\) (ideal metal model\(^8,9\)), where the finite jellium has an infinitesimally thin dipole layer on its surface. The relation (5.11) provides the strength of the dipole layer at equilibrium $[P_e(n_0) = 0]$ of a metal in the vacuum: $D(n_0) = [n_0\partial \epsilon_1/\partial n]_0$, which is identical with the result determined from the SJ model. In the SJ model the strength of the dipole layer is assumed to be given by the relation:

$$D(n) = \frac{n}{n_0}D(n_0) .$$

With use of this approximation the electron pressure in a liquid metal can be determined finally by

$$P_e(n) = n^2 \left[ \frac{\partial \epsilon_1}{\partial n} - \frac{\partial \epsilon_1}{\partial n_0} \right].$$

On the other hand, Nieminen and Hodge\(^38\) showed that application of the relation (5.6) to a free electron of plane waves leads to the expression for the pressure in terms of the internal chemical potential $\bar{\mu}$:

$$P_e(n) = n(\bar{\mu} - \epsilon_3) ,$$

which can be also derived by the TF theory with the Weizsacher correction\(^24,26,39,40\). At this point, Eq. (5.14) can be rewritten in the form:

$$P_e = n(\bar{\mu} - \mu_3) + n^2\frac{d\epsilon_1}{dn}$$

with $\mu_3 = d(n\epsilon_3)/dn$. By comparing this equation with (5.11) we obtain the following relation:

$$D = \mu_3 - \bar{\mu} ,$$

which leads to the formula for work function $w$:\(^41\) $w = D - \mu_3 = -\bar{\mu}$ with $\mu_3$ providing the internal chemical potential. From this equation we see that the relation $-D/n = (\bar{\mu} - \mu_3)/n = -d\epsilon_1/\partial n|_{n_0}$ is assumed in the SJ model.

It has been already discussed about the problem that the electron pressure for a plasma does not become zero at equilibrium in the vacuum: in fact, in constructing the EOS for a plasma by the use of the ion-sphere model based on the TF method, a similar correction to (5.13) is introduced as a chemical bonding correction (Barnes correction) to make the electron pressure zero at equilibrium in the vacuum by More \textit{et al.}\(^42\). In the same spirit, we adopt (5.13) as the electron pressure $P_e$ in (5.4); then, the total pressure for liquid metals is described in the final form:

$$P = n^2 \left[ \frac{\partial \epsilon_1}{\partial n} - \frac{\partial \epsilon_1}{\partial n_0} \right] + n_0k_BT - \frac{1}{6}(n_0^1)^2\int g_{\Pi}(r)\nabla v_{H_{\Pi}}^\text{eff}(r)dr .$$

At this point, it should be noticed that the following relation

$$n_0^1k_BT = \frac{1}{6}(n_0^1)^2\int g_{\Pi}(r)\nabla v_{H_{\Pi}}^\text{eff}(r)dr$$

must be satisfied at equilibrium in the vacuum, where $P_N = 0$. 

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5.2. Numerical examination of the QHNC equation by the zero-pressure condition

In this subsection, we exhibit how the zero-pressure condition, (5.18), can be used as a check of numerical consistency in the calculation by applying it to some alkaline liquid metals at the normal pressure on the basis of the QHNC equation as an example. Since we can regard liquid metals at the normal pressure as those in the vacuum, the pressures determined from (5.17) must be zero in this circumstance: that is, $P_N = 0$ while $P_e = 0$ by definition. In order to examine this relation we calculated the nuclear virial term and nuclear kinetic pressures from (5.17), which are shown in Table I for Li, Na and Rb.

In the case of Li, the nuclear virial term becomes -0.2871 GPa, which provides almost zero total pressure 0.0017 GPa by canceling out the nuclear kinetic pressure 0.2888 GPa. Thus, the QHNC equation can be considered to give a reasonable result for Li to fulfill (5.18) in comparison with -1.7 GPa of Kumaravadivel. However, the QHNC equation does not provide even negative values of the nuclear virial term for the Na and Rb cases; as a result, the nuclear pressure remains to be a large positive value for each case.

To see where this discrepancy comes from, we calculated the pressure of Rb from an effective ion-ion interaction determined by the Ashcroft model potential with the core parameter $r_c = 1.27\text{Å}^{36}$ on the basis of (5.17): the nuclear pressure becomes -0.0013 GPa, which satisfies the condition (5.18) to a considerable extent compared to other calculation shown in Table I. Inversely, the condition (5.18) can be used to determine the Ashcroft core parameter $r_c$; this condition generates $r_c = 1.275\text{Å}$ for Rb case. In Fig. 1, the effective ion-ion interactions for a Rb liquid metal obtained from the Ashcroft model with $r_c = 1.275\text{Å}$ are plotted together with that from the QHNC method. Although we find a visible difference between these

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The effective ion-ion interactions of Rb (313K) determined by the QHNC equation and by the use of Ashcroft model potential ($r_c = 1.275$), which are shown by the full and dotted curves, respectively.}
\end{figure}
two effective potentials in this scale, these potentials yield almost the same structure factors showing a good agreement with experiments as is displayed in Fig. 2. In contrast to the Ashcroft model potential, the pseudopotential \(-C_{el}(r)/\beta\) determined from the QHNC equation has a complicate inner structure in the core region. As a consequence, the term \(\int C_{el}^{R}(r)dr\) [\(C_{el}^{R}(r)\): the non-Coulomb part] which appears in (5.18) is difficult to calculate with a sufficient accuracy; the discrepancy of the QHNC result for the zero-pressure condition is attributed to this problem in the Rb and Na cases in contrast to the case of a Li metal which has a simpler inner core structure in the pseudopotential \(C_{el}\). It is well known that the inner-core structure of a pseudopotential is not significant to determine the effective ion-ion interaction, but is important to calculate the thermodynamical quantities, as the QHNC results indicate. It is worth noting that the condition (5.18) provides a check of numerical consistency in the calculation for determining the effective ion-ion interaction, the structure factor and the thermodynamical quantities for a liquid metal in the vacuum.

§6. Summary and discussion

In general, the virial theorem (2.10) teaches us that the partial pressure associated with each component in a mixture can be uniquely defined by using the wall potential for each component, and the total pressure is represented as a sum of them: this definition is assured by the virial theorem for single particle, (2.13) and (2.14). Also, the partial pressure can be actually measured as an osmotic pressure, for example. Therefore, in an electron-nucleus mixture, the electron and nuclear pressures

![Fig. 2. The ion-ion structure factors \(S_{III}(Q)\) of Rb obtained by use of the effective ion-ion interactions based on the QHNC and Ashcroft models, which are displayed by the full and dotted curves, respectively. The full and white circles indicate the experimental results by the neutron\(^{45}\) and X-ray\(^{46}\) diffraction methods, respectively. The Ashcroft model with \(r_c = 1.275\)Å determined by the condition \(P_N = 0\) provides an indistinguishable structure factor from the QHNC result in a good agreement with the experiments.](image)
Electron and nuclear pressures

are clearly and simply defined as the partial pressures owing to the virial theorem as is shown in §2, and the thermodynamic pressure of this system is given by a sum of the electron and nuclear pressures. To be consistent with this fact, the electron pressure in this mixture is defined by

\[ P_e \equiv 2 \langle T_e \rangle - \sum_i \langle \hat{r}_i \cdot \nabla_i U \rangle = 2 \langle T_e \rangle_N + \langle U_e \rangle_N - \sum_\alpha \langle \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \rangle_N, \quad (6.1) \]

which makes a contrast to another definition in terms of the forces on the nuclei

\[ P_e \equiv \sum_\alpha \langle \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \rangle_N = 2 \langle T_e \rangle_N + \langle U_e \rangle_N. \quad (6.2) \]

It should be pointed out that the pressure represented by (6.2) is neither the electron pressure nor the total pressure for this system, and that this pressure is associated with the total pressure of another inhomogeneous system (System-II as is named in §2), where only the nuclei are confined in the volume and the electron can move over all space under the external potential caused by the confined nuclei. Similar remarks are made about the definition of the stress tensor for this mixture as is discussed in §3.

In §4, we have enumerated several kinds of definitions for the electron pressure, which lead to the electron-pressure expression (6.1), where the nuclear virial term is subtracted. It is important for the calculation of the total pressure by adding the nuclear pressure that we should recognize which definition is adopted to determine the electron pressure. For example as was shown by (4.15), the electron pressure calculated by use of the surface integral expression, \[ \tilde{P}_e V = \oint_{\partial \mathbf{V}_N} \mathbf{r} \cdot \tilde{P}_e \cdot d\mathbf{S} \], is different from the pressure determined on the basis of the relation, \[ \tilde{P}_e V = 2T_e[n] + E_{es}[n] + \int_{\mathbf{r}} \text{tr} \mathbf{P}_{xc} d\mathbf{r} \], in that the latter contains a part of the nuclear pressure \[ \sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \], which is approximated by the Madelung energy term: \[ NCZ_{out}^2/4a \] as is given by Janak.

When the nuclei behave as classical particles, the partition function of an electron-nucleus mixture with the Hamiltonian (2.1) is written exactly in the form

\[ Z_N = \frac{1}{N! h^{3N}} \int d\mathbf{R}^N \int d\mathbf{P}^N \exp \left[ -\beta \left( \sum_\alpha \frac{\mathbf{P}_\alpha^2}{2M} + F_e[n; \{ \mathbf{R}_\alpha \}] \right) \right], \quad (6.3) \]

where the electron free energy \[ F_e[n; \{ \mathbf{R}_\alpha \}] \] defined by (4.2) plays a role of a many-body interaction among the nuclei: \[ \alpha \]

\[ \mathbf{F}_\alpha = -\nabla_{\alpha} F_e|_{TV_N} = -\nabla_{\alpha} E_{es}|_{n(r)} \]

\[ = Ze^2 \int n(r) \frac{\mathbf{r} - \mathbf{R}_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|^3} d\mathbf{r} + (Ze)^2 \sum_{\alpha \neq \gamma} \frac{\mathbf{R}_\alpha - \mathbf{R}_\gamma}{|\mathbf{R}_\alpha - \mathbf{R}_\gamma|^3}. \quad (6.4) \]

Thus, the pressure of this system is obtained by performing the volume derivative of the free energy \[ F = -k_B T \ln Z_N \] without use of any approximation in the form

\[ 3PV = -3V \frac{\partial F}{\partial V} \Big|_{TN} = \left\langle -3V \frac{\partial F_e}{\partial V} \right\rangle_N + 3Nk_B T + \left\langle \sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \right\rangle_N, \quad (6.6) \]
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which is identical with (5.2); this relates the electron pressure determined in §4 under the adiabatic approximation to the total pressure and to that by the virial theorem (5.1) owing to (4.1). That is, the relation, \( P = P_e + P_N \), is proven without use of the wall potentials by (6.6) in the adiabatic approximation.\(^{10}\) When we approximate \( F_e \) involved in (6.3) as

\[
F_e[n; \{ R_\alpha \}] \approx U_0(V) + \frac{1}{2} \sum_{\alpha \neq \beta} v_{eff}^H(|R_\alpha - R_\beta|), \quad (6.7)
\]

and perform the volume derivative of \( F \), we obtain the standard virial EOS\(^{36}\) for simple liquid metals. On the other hand, the virial EOS (5.17) is derived by applying the approximation (6.7) only to the nuclear virial term of (6.6); the first term of (6.6) is treated appropriately as the electron pressure in contrast with the standard virial formula,\(^{36}\) in which derivation the approximation (6.7) is applied to both terms involving \( F_e \) in (6.6). As a result, the electron pressure in the exact expression (6.6) becomes to be represented by

\[
P_e \approx (n_0^1)^2 \frac{dU_0(n_0^1)}{dn_0^1} + \frac{1}{2} (n_0^1)^3 \int g_{II}(r) \frac{\partial v_{eff}^H(r)}{\partial n_0^1} d\mathbf{r}, \quad (6.8)
\]

in the standard virial formula for a liquid metal. Therefore, the EOS (5.17) is more accurate than the standard virial formula in spite of its simpler structure.

A metal in the vacuum is defined as an electron-nucleus mixture without the wall potentials, which confine the electrons \( (U_{ele})^w \) and the nuclei \( (U_{nuc})^w \) in a finite volume. From this definition, we can give another important remark that the zero pressure of an electron-nucleus mixture in the vacuum is realized by both electron and nuclear pressures being zero at the same time: this can also be verified directly from thermodynamics as described in Appendix A. In the adiabatic approximation, the electron pressure is given by thermodynamics in the form

\[
3P_e V \equiv - \left\langle 3V \frac{\partial F_e[n; \{ R_\alpha \}]}{\partial V} \right\rangle_N = \left\langle \{ 2T_e + U_e - \sum_\alpha R_\alpha \cdot F_\alpha \} \right\rangle_N = 2\langle \hat{T}_e \rangle - \sum_i \langle \hat{r}_i \cdot \nabla \hat{U} \rangle, \quad (6.9)
\]

which is zero in the vacuum due to (2.13), since a metal in the vacuum is not confined by the wall. Similarly, \( P_N = 0 \) due to (2.14). Therefore, in the first-principles molecular dynamics (MD) performed on liquid metals in the vacuum, for example, the nuclear pressure should become zero \( (P_N = 0) \); this relation also can be used to check numerical consistency in the MD calculation.

**Appendix A**

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**Electron pressure determined by the DF theory**---

The electron pressure can be expressed in terms of the internal energy of the interacting electrons in the presence of the external potential caused by the fixed
electron and nuclear pressures

nuclei at \{R_\alpha\} as follows:\(^{10}\)

\[
\tilde{P}_e \equiv -\frac{\partial F_{\text{DF}}}{\partial V}_{\text{TN}_e(R_\alpha)} = -\frac{\partial E_V}{\partial V}_{\text{SN}_e(R_\alpha)} .
\]  

(A-1)

In the DF theory, this electron internal energy is written as

\[
E^V[n; \{R_\alpha\}] \equiv T_s^V[n] + E_{\text{es}}^V[n; \{R_\alpha\}] + E_{\text{xc}}^V[n] .
\]  

(A-2)

Here, the exchange-correlation part of the internal energy is defined by

\[
E_{\text{xc}}^V[n] \equiv F_{\text{xc}}[n] - T \frac{\partial F_{\text{xc}}[n]}{\partial T} \bigg|_{V n(r)} ,
\]  

(A-3)

and the kinetic-energy functional \(T_s^V[n]\) and the electrostatic energy \(E_{\text{es}}^V[n; \{R_\alpha\}]\) of this system are given by \((4.24)\) and \((3.7)\), respectively. With use of the scaled electron density distribution \(n_\lambda(r) \equiv \lambda^3 n(\lambda r)\), the electron pressure \(\tilde{P}_e\) for this system can be determined by \(\lambda\) derivative in the form:

\[
3\tilde{P}_e V = -3V \frac{\partial E_V[n; \{R_\alpha\}]}{\partial V} \bigg|_{N_e} = \lambda \frac{\partial E_\lambda}{\partial \lambda} \bigg|_{\lambda=1} ,
\]  

(A-4)

with

\[
E_\lambda \equiv E^{V/\lambda^3}[n_\lambda; \{R_\alpha\}] = T_s^{V/\lambda^3}[n_\lambda] + E_{\text{es}}^{V/\lambda^3}[n_\lambda; \{R_\alpha\}] + E_{\text{xc}}^{V/\lambda^3}[n_\lambda] .
\]  

(A-5)

In the above, the scaled density distribution \(n_\lambda(r)\) keeps the total electron number as a constant in the \(\lambda\)-variation: \(N_e = \int_V n(r) d\mathbf{r} = \int_{V/\lambda^3} n_\lambda(r) d\mathbf{r}\). With use of the following relations

\[
T_s^{V/\lambda^3}[n_\lambda] = \lambda^2 T_s^V[n] ,
\]  

(A-6)

\[
E_{\text{es}}^{V/\lambda^3}[n_\lambda; \{R_\alpha\}] = \lambda E_{\text{es}}^V[n; \{\lambda R_\alpha\}] ,
\]  

(A-7)

and the exchange-correlation contribution\(^{27}\)

\[
\lambda \frac{\partial E_{\text{xc}}^{V/\lambda^3}[n_\lambda]}{\partial \lambda} \bigg|_{\lambda=1} = -\int_V n(r) \mathbf{r} \cdot \nabla \frac{\delta F_{\text{xc}}}{\delta n(r)} \bigg|_{T^V} d\mathbf{r} + \oint_{\partial V} \mathbf{r} \cdot \mathbf{F}_{\text{DF}} d\mathbf{S} = \int_V \text{tr} \mathbf{F}_{\text{xc}} d\mathbf{r} ,
\]  

(A-8)

we get finally the expression for the electron pressure in the form:

\[
3\tilde{P}_e V = \lambda \frac{\partial E_\lambda}{\partial \lambda} \bigg|_{\lambda=1} = 2T_s^V[n] + E_{\text{es}}^V + \int_V \text{tr} \mathbf{F}_{\text{xc}} d\mathbf{r} - \sum_\alpha R_\alpha \cdot F_\alpha
\]  

(A-9)

\[
= 2T_e + U_e - \sum_\alpha R_\alpha \cdot F_\alpha ,
\]  

(A-10)

in terms of the true kinetic and potential energies given by \(T_e = T_s^V[n] + T_{\text{xc}}\) and \(U_e = E_{\text{es}}^V + U_{\text{xc}}\), respectively. Here, the exchange-correlation contributions to the kinetic and potential energies, \(T_{\text{xc}}\) and \(U_{\text{xc}}\), are defined by the relations

\[
2T_{\text{xc}} + U_{\text{xc}} = \int_V \text{tr} \mathbf{F}_{\text{xc}} d\mathbf{r} ,
\]  

(A-11)

\[
T_{\text{xc}} + U_{\text{xc}} = E_{\text{xc}}^V .
\]  

(A-12)
On the other hand, in the adiabatic approximation, we have an average relation,
\[ \langle \hat{A} \rangle = \langle \langle \hat{A} \rangle \rangle_E \]
where the bracket with a suffix \( e \) denotes the average over the electron states at a fixed nuclear configuration. Therefore, with use of this approximation and (A.10), the electron pressure (2.19) defined by the virial theorem can be written as
\[
2\langle \hat{T}_e \rangle - \sum_i \langle \hat{r}_i \cdot \nabla \hat{U} \rangle = \{ \langle 2\hat{T}_e \rangle + \langle \hat{U} \rangle - \sum_{\alpha} \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \} \}_N \]
which is identical with (4.15). It is important to note that the nuclei are fixed at the positions \( \{ \mathbf{R}_\alpha \} \) when the volume derivative is performed to determine the electron pressure.

**Appendix B**

**Criticism on the Janak derivation of the pressure formula**

In the DF theory for the electron gas confined in the volume \( V \) [System-I], the kinetic energy \( T_s[n] \) is written as
\[
2T_s[n] = -\int_V \mathbf{r} \cdot \nabla \cdot \mathbf{P}^{DF}_K \, d\mathbf{r} + \oint_{\partial V} \mathbf{r} \cdot \mathbf{P}^{DF}_K \cdot d\mathbf{S} = \int_V \text{tr} \mathbf{P}^{DF}_K \, d\mathbf{r} \]
\[
= \int_V n(r) \mathbf{r} \cdot \nabla U_{\text{eff}}(r) \, d\mathbf{r} + \oint_{\partial V} \mathbf{r} \cdot \mathbf{P}^{DF}_K \cdot d\mathbf{S},
\]
in terms of the kinetic pressure tensor \( \mathbf{P}^{DF}_K \) defined by \( \nabla \cdot \mathbf{P}^{DF}_K = -n(r) \nabla U_{\text{eff}}(r) \). Also, the exchange-correlation pressure tensor \( \mathbf{P}_{xc} \), which is defined by the relation:
\[
\nabla \cdot \mathbf{P}_{xc} \equiv n(r) \nabla \delta E_{xc}/\delta n(r),
\]
satisfies
\[
\int_V \text{tr} \mathbf{P}_{xc} \, d\mathbf{r} = -\int_V \mathbf{r} \cdot \nabla \cdot \mathbf{P}_{xc} \, d\mathbf{r} + \oint_{\partial V} \mathbf{r} \cdot \mathbf{P}_{xc} \cdot d\mathbf{S}
\]
\[
= -\int_V n(r) \mathbf{r} \cdot \nabla \delta E_{xc}/\delta n(r) \, d\mathbf{r} + \oint_{\partial V} \mathbf{r} \cdot \mathbf{P}_{xc} \cdot d\mathbf{S}.
\]

Note that Eqs. \([B.1]\) and \([B.3]\) are a general relation which must be satisfied for any tensor in the electron gas confined in the volume \( V \). Nevertheless, the surface integrals in \([B.2]\) and \([B.4]\) are neglected in Janak’s equations, \(1) \) \( (7) \) \( \) \( \) \( \) \( and (10) \) in the local-density approximation, respectively.

Since the electrostatic energy \( E_{es} \), \([B.7]\), fulfills the following relation:\(10)\)
\[
E_{es} - \sum \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha = -\int_V n(r) \mathbf{r} \cdot \nabla \delta E_{es}/\delta n(r) \, d\mathbf{r},
\]
with the force \( \mathbf{F}_\alpha \equiv -\nabla \alpha E_{es} \) on the \( \alpha \)th nucleus, and the effective external potential is defined by \( U_{\text{eff}}(r) = \delta [E_{es} + E_{xc}] / \delta n(r) \), Janak has derived from \([B.2]\) and \([B.4]\)
\[
\int_{\partial V} \mathbf{r} \cdot (\mathbf{P}^{DF}_K + \mathbf{P}_{xc}) \cdot d\mathbf{S} + \sum \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha = 2T_s[n] + E_{es} + \int_V \text{tr} \mathbf{P}_{xc} \, d\mathbf{r}
\]
\[
= 2T_e + U_e,
\]
with *neglect* of the surface-integral term in (B.6) as mentioned before. If we put

$$3PV = \sum R_\alpha \cdot F_\alpha$$

in (B.6) as Janak defined, we obtain

$$3PV = 2T_e + E_e + \int_V \text{tr}P_{xc}dr - \oint_{\partial V} r \cdot (P^D_K + P_{xc}) \cdot dS.$$  (B.8)

Therefore, this pressure definition provides neither the electron pressure nor the total pressure of System-I in the Janak derivation. On the other hand, if we put in the above

$$3\tilde{P}_eV = \oint_{\partial V} r \cdot (P^D_K + P_{xc}) \cdot dS = 2T_e + U_e - \sum R_\alpha \cdot F_\alpha = 0,$$  (B.9)

the pressure given by (B.8) becomes the total pressure of System-II with infinite nuclear mass. In contrast with the above fact, Eq. (B.6) with the surface-integral term is identical with (4.15) or (2.9): the sum of the electron and nuclear pressures are equal to the total pressure of System-I with infinite nuclear mass. In reality, Janak’s pressure formula for numerical calculation becomes that of System-I, since the surface-integral terms in (B.2) and (B.4), in comparison with his equation (7), are taken into account in his equation (23) at this stage.

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