Unified description of metallic and neutral liquids and plasmas

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Abstract. A formulation to evaluate equilibrium properties of a non-simple metallic liquid and plasma is presented in a unified fashion involving a neutral liquid as a special case; a multi-centre problem is to be solved in a coupled manner with a single-centre problem in this formulation. A liquid metal or a plasma is taken as a binary mixture of nuclei and electrons. Firstly, an inhomogeneous nucleus–electron mixture caused by fixing a nucleus at the origin is investigated by the density-functional theory for a single-centre problem to determine the internal electronic structure of an ion at the origin, which enables us to think of a liquid metal as an ion–electron mixture composed of ions with the same electronic structure as the central ion so built up at the origin. Thus, the radial distribution functions, a self-consistent potential for electrons and the ionic charge are obtained, if the bare ion–ion interaction is given beforehand; these quantities are used to solve the following multi-centre problem. Secondly, the problem of treating a homogeneous nucleus–electron mixture is reduced to the multi-centre problem of an inhomogeneous electron gas under the external potential caused by randomly distributed nuclei. Thus, this system is shown to be regarded as a classical one-component fluid described by an effective Hamiltonian, with the same interparticle potential as the effective interionic interaction obtained in the previous single-centre problem; a bare ion–ion interaction is now created by an extension of the Gordon–Kim (GK) or tight-binding bond (TBB) model. This formulation offers a generalization of the GK and TBB methods to take account of the presence of the conduction electrons with use of self-consistent bound-state functions in a liquid. Here, a bound state is defined as a state with a negative eigenvalue or a resonant state with a long lifetime. The internal energy of a liquid metal is expressed in terms of output from the single-centre problem based on the nucleus–electron model.

1. Introduction

In the standard approach, a liquid metal is considered as a quasi-one-component liquid interacting via an effective potential determined by the electron theory with use of a pseudopotential. However, we can not deal with a plasma by this approach, since a pseudopotential is not able to be built up in the wide range of temperatures and densities within the standard pseudopotential theory. Therefore, it is natural to think of a liquid metal or a plasma as composed of ions and electrons. In this point of view, there arises a fundamental question of what is an 'ion' in a liquid metal or a plasma in a generalized meaning applicable to any metallic system, although in a simple metal we have a clear image of an 'ion'. We have no general definition of a ionic charge Z_I applicable to a non-simple metallic system where the core-electron

overlap is non-negligible, and resonant states play an important role to construct an ion. In other words, the ionization of a plasma, for example, has not been defined in the form applicable for general situations to date. In spite of this fact, a liquid metal or a plasma can be modelled as a binary mixture of ions and electrons, when the ionic charge Z_I and interparticle interactions $v_{ij}(r)$ are assumed to be all known beforehand. On the basis of the ion–electron model for a liquid metal, a set of integral equations for the radial distribution functions (RDF) has been set up in the quantal hypernetted chain (QHNC) approximation within the framework of the density-functional (DF) theory [1]. There is only a proton–electron system, the interparticle potentials $v_{ij}(r)$ of which are all known beforehand as an ion–electron mixture; the QHNC formulation was applied to a hydrogen plasma with a perfectly ionization [2] and to a liquid metallic hydrogen [3]. On the other hand, with the help of the DF theory, Dharma-wardana and Perrot [4] derived a set of integral equations for the RDFs in a strongly coupled plasma taking the ion–ion correlation in the HNC approximation, and applied them to a hydrogen plasma. However, it is shown that their formulation cannot deal with a liquid metal or a plasma with significant core electrons due to their poor approximation for the electron–ion correlation [5].

In order to treat a liquid metal with core electrons by the QHNC formulation for the ion–electron mixture, the bare electron–ion interaction $v_{eI}(r)$ and its ionic charge Z_I are necessary to be obtained by another method, even when the bound-electron core is so small and rigid that the bare ion–ion interaction is taken approximately to be purely Coulombic. For this purpose, a liquid metal is more fundamentally considered as a nucleus–electron mixture, and thus, the expressions for $v_{eI}(r)$ and Z_I are obtained to be used in the ion–electron model [6]; this formulation was applied to a liquid metallic lithium, and was shown to be capable of giving the liquid structure [7] and the internal electronic structure [8] of an ion observed by K-edge position in excellent agreements with experiments of Li. As a consequence, this formulation is expected to be applicable to any other simple metallic system, where the core-overlap effect and resonant states are negligible. Obviously, the QHNC formulation need to be generalized in some points to treat non-simple metallic systems, however. In this connection, there is a simple and powerful method proposed by Gordon and Kim [9] to evaluate the core-overlap interaction between two atoms or two ion in the vacuum. Later on, Harris [10] extended the Gordon–Kim method to allow a description of bonding in general by treating the kinetic energy more exactly than the Thomas–Fermi approximation. However, the bare ion–ion interaction in a liquid metal can not be derived by these methods, which yield good results only for an interaction caused by the bound electrons contained in two atoms in the circumstance where the contribution of the conduction electrons is negligible.

In the determination of the equilibrium properties of a liquid metal or a plasma, two types of problems are usually set up: the single-centre and multi-centre problems. In a liquid metal, the ion–ion and electron–ion RDFs are identical with the electron and ion density distributions around a fixed ion in the ion–electron mixture; thus, the problem to determine the RDFs concerning ion constitutes a single-centre problem to evaluate the electron- and ion-density distributions in the inhomogeneous ion–electron mixture caused by a fixed ion at the origin. On the other hand, to obtain the density of states and thermodynamic quantities such as the internal energy or the pressure of a liquid metal we must struggle with a multi-centre problem of the inhomogeneous electron gas produced by randomly distributed ions. In the standard procedure to deal with a liquid metal, these two problems are treated quit independently of each

other, and their interrelation is not clearly understood even now. For example, at the present stage it is a matter of discussion whether the ionization of a plasma should be defined by treating the single-centre problem or the multi-centre problem.

The layout of the present paper is as follows. In section 2 the QHNC formulation for the ion–electron mixture is summarised, and the approximations involved in it is explicitly stated to clarify the problem of the QHNC approach to treat the conduction electrons. Also, as an approach to treat the bound-electron contribution the Gordon–Kim method and Harris' extension are described in conjunction with their limit of applicability. In section 3, a formulation to treat a non-simple metallic system is presented in a coupled form of the single- and multi-centre problems, and their interrelation is considered there. The last section is devoted to a summary and discussion.

2. Previous results and their problems

2.1. The ion–electron model and simple metallic systems

Usually, a liquid metal or a plasma is taken as a mixture of ions and electrons. To get a clear meaning of an ion–electron mixture, let us consider a binary mixture consisting of one kind of ions with a definite ionic charge Z_I and the conduction electrons, interacting with each other via *binary* potentials $v_{ij}(r)$ $[i, j = I$ or $e]$; the ions are assumed to behave as *classical* particles in the sense that their coordinates R_i and momenta P_i are commutable, while the conduction electrons form a quantum fluid, and are clearly distinct from the bound-electrons forming an ion. Then, we can think of this mixture as a model for a liquid metal or a plasma with uniform density n_0^I and electron density $n_0^e = Z_I n_0^I$ [referred to as the ion–electron model]. In this model, the ion–ion and electron–ion RDFs, $g_{II}(r)$ and $g_{eI}(r)$, are identical with the ion- and electron-density distributions, $n_I(r|I)/n_0^I$ and $n_e(r|I)/n_0^e$, around a fixed ion in the mixture, respectively. Since an ion fixed at the origin causes external potentials $U_i(r) = v_{iI}(r)$ acting on ions $(i = I)$ and electrons $(i = e)$, the RDFs become equal with the inhomogeneous density distributions $n_i(r|\{U_\alpha = v_{\alpha I}\})/n_0^i$ under external potentials $U_i(r) = v_{iI}(r)$ applied to the homogeneous ion–electron mixture

$$g_{iI}(r) = n_i(r|I)/n_0^i = n_i(r|\{U_\alpha = v_{\alpha I}\})/n_0^i . \tag{2.1}$$

These relations can be proved by using the fact that the ions are classical particles in a similar manner that Percus [11] derived the above relation for a pure classical liquid (see the appendix for details).

The above fundamental relations (2.1) give a clue to the evaluation of the RDFs on the basis of the DF theory [1], which can afford to give exact expressions for the inhomogeneous density distributions $n_i(r|U_I U_e)$ induced by external potentials $\{U_I, U_e\}$ applied to the homogeneous mixture. In the DF theory, the effective external potentials to evaluate the density distributions $n_i(r|U_I U_e)$ under the external potentials $U_i(r)$ are defined in such a way that the density distributions $n_i^0(r|U_i^{eff})$ of noninteracting systems under effective external potentials U_i^{eff} should become identical with the density distributions $n_i(r|U_I U_e)$ of the real system: $n_i^0(\mathbf{r}|U_i^{eff}) \equiv n_i(\mathbf{r}|U_I U_e)$, and are shown to be given exactly by $U_i^{eff}(r) = U_i(r) + \delta \mathcal{F}_{int}/\delta n_i(r) - \mu_i^{int}$ in terms of the interaction part of the intrinsic free-energy $\mathcal{F}_{int}$ and $\mu_i^{int} \equiv \mu_i - \mu_i^0$. Here, μ_i

and μ_i^0 are chemical potentials of interacting and noninteracting systems of i-kind particles, respectively. In this way, the DF theory can reduce exactly a *many*-body problem to determine the density distribution $n_i(r|U_I U_e)$ of the interacting mixture in the presence of the external potential $\{U_I, U_e\}$ to a *one*-body problem to calculate the density distribution $n_i^0(r|U_i^{eff})$ in the noninteracting particles under the effective external potential $U_i^{eff}(r)$. As a result, the DF theory provides the formal, but *exact* expressions for the RDFs $g_{iI}(r)$ concerning ion as follows [3]

$$g_{iI}(r) = n_i(r|\{U_\alpha = v_{\alpha I}\})/n_0^i = n_i^0(r|U_i^{eff})/n_0^i \qquad (2.2)$$

with

$$U_i^{eff}(r) = v_{iI}(r) + \frac{\delta \mathcal{F}_{int}}{\delta n_i(r|I)} - \mu_i^{int} \qquad (2.3)$$

$$= v_{iI}(r) - \frac{1}{\beta} \sum_\ell \int C_{i\ell}(|r - r'|) \, n_0^\ell [g_{\ell I}(r') - 1] \, dr' - B_{iI}(r)/\beta \qquad (2.4)$$

in terms of the bridge functions $B_{iI}(r)$ and the direct correlation functions (DCF) $C_{ij}(r)$. Here, $n_i^0(r|U_i)$ denotes the density distribution of the non-interacting particles of kind i; $n_I^0(r|U_I) = n_0^I \exp(-\beta U_I(r))$ for ions, while the non-interacting electron density $n_e^0(r|U_e)$ can be determined by solving the wave equation for an electron under the external potential $U_e(r)$. In the above expression, the DCF $C_{ij}(r)$ in the ion–electron mixture are defined within the framework of the DF theory by

$$C_{ij}(|r - r'|) \equiv -\beta \frac{\delta^2 \mathcal{F}_{int}[n_I, n_e]}{\delta n_i(r) \delta n_j(r')}\Big|_0 = \beta \frac{\delta[\mu_i^0 - U_i^{eff}(r)]}{\delta n_j^0(r')}\Big|_0 - \beta \frac{\delta[\mu_i - U_i(r)]}{\delta n_j(r')}\Big|_0 \qquad (2.5)$$

where the suffix 0 denotes the functional derivative at the uniform densities [1]. Actually the explicit expression for the DCF are given by the Fourier transform in the matrix form

$$\sqrt{\mathcal{N}} C(Q) \sqrt{\mathcal{N}} = (\tilde{\chi}_Q^0)^{-1} - (\tilde{\chi}_Q)^{-1} \qquad (2.6)$$

in terms of the density response functions, $\tilde{\chi}_Q \equiv \| \chi_{ij}(Q) \|$ and $\tilde{\chi}_Q^0 \equiv \| \chi^{0i}(Q) \delta_{ij} \|$, of the interacting and non-interacting systems, respectively, with $\mathcal{N} \equiv \| n_0^i \delta_{ij} \|$. This relation results from (2.5) by noting that the density–density response functions $\chi_{ij}(Q)$ are defined by

$$\chi_{ij}(Q) \equiv \frac{\langle \delta \hat{\rho}_i(Q); \delta \hat{\rho}_j^*(Q) \rangle}{\sqrt{N_i N_j}} = \frac{1}{\sqrt{n_0^i n_0^j}} \mathcal{F}_Q \left[\frac{\delta n_i(r)}{\beta \delta[\mu_j - U_j(r')]}\Big|_0 \right] \qquad (2.7)$$

with $\delta \hat{\rho}_i(Q) = \sum_\ell \exp(iQ \cdot \hat{r}_\ell^i) - N_i \delta_{Q,0}$ and the total number N_i of i-kind particle. Here, $\mathcal{F}_Q[f(r)] \equiv \int e^{iQ \cdot r} f(r) \, dr$ and $\langle X; Y \rangle$ is the canonical correlation defined by Kubo [12]

$$\langle X; Y \rangle \equiv \frac{1}{\beta} \int_0^\beta \left\langle \exp\left[\lambda\left(\hat{H} - \sum_i \mu_i \hat{N}_i\right)\right] X \exp\left[-\lambda\left(\hat{H} - \sum_i \mu_i \hat{N}_i\right)\right] Y \right\rangle d\lambda \qquad (2.8)$$

with the total Hamiltonian $\hat{H}$ and the total number operator $\hat{N}_i$ of the kind i particle

Note here that the density–density response functions $\chi_{iI}(Q)$ concerning ion become identical with structure factors $S_{iI}(Q)$ and $\chi^{0I}(Q) = 1$, since the canonical correlation reduces to the usual correlation: $\langle \delta\hat{\rho}_i(Q); \delta\hat{\rho}_I^*(Q)\rangle = \langle\delta\hat{\rho}_i(Q)\delta\hat{\rho}_I^*(Q)\rangle \equiv S_{iI}(Q)\sqrt{N_iN_I}$, because of $[\hat{P}_i,\hat{R}_i] = 0$ in the canonical correlation (2.8) if the ions behave as classical particles. Therefore, the structure factors concerning ion in the ion–electron mixture can be described in terms of the DCF $C_{ij}(Q)$ from (2.6)

$$S_{II}(Q) = [1 - n_0^e C_{ee}(Q)\chi_Q^0]/D(Q) \tag{2.9}$$

$$S_{eI}(Q) = \sqrt{n_0^I n_0^e}\, C_{eI}(Q)\chi_Q^0/D(Q) \tag{2.10}$$

$$= \frac{\rho(Q)}{\sqrt{Z_I}} S_{II}(Q) \tag{2.11}$$

where

$$\rho(Q) \equiv \frac{n_0^e C_{eI}(Q)\chi_Q^0}{1 - n_0^e C_{ee}(Q)\chi_Q^0} \tag{2.12}$$

$$D(Q) \equiv [1 - n_0^I C_{II}(Q)][1 - n_0^e C_{ee}(Q)\chi_Q^0] - n_0^I n_0^e |C_{eI}(Q)|^2 \chi_Q^0 \tag{2.13}$$

with $\chi_Q^0 = \chi^{0e}(Q)$. At this point, it is interesting to note that the inverse Fourier transform of (2.11) leads to the relation:

$$n_0^e g_{eI}(r) = \rho(r) + n_0^I \int \rho(|r - r'|)\, g_{II}(r')r' \tag{2.14}$$

which states that the conduction-electron distribution $n_0^e g_{eI}(r)$ around the fixed ion in the ion–electron mixture can be described exactly by the superposition of surrounding 'neutral pseudoatoms', each of which carries about a screening cloud $\rho(r)$. Also, the Ornstein–Zernike (OZ) relations in the ion–electron mixture are obtained from the inverse Fourier transform of the matrix identity

$$(\tilde{\chi}_Q)(\tilde{\chi}_Q^0)^{-1} - 1 = (\tilde{\chi}_Q^0)\sqrt{\mathcal{N}}C(Q)\sqrt{\mathcal{N}} + (\tilde{\chi}_Q^0)\sqrt{\mathcal{N}}C(Q)\sqrt{\mathcal{N}}\left((\tilde{\chi}_Q)(\tilde{\chi}_Q^0)^{-1} - 1\right)$$

in the forms

$$g_{II}(r) - 1 = C_{II}(r) + \Gamma_{II}(r) \tag{2.15}$$

$$g_{eI}(r) - 1 = \hat{B}C_{eI}(r) + \hat{B}\Gamma_{eI}(r) \tag{2.16}$$

with

$$\Gamma_{ij}(r) \equiv \sum_\ell \int C_{i\ell}(|r - r'|)\, n_0^\ell[g_{\ell j}(r') - 1]\, dr' \tag{2.17}$$

where $\hat{B}$ denotes an operator defined by $\mathcal{F}_Q[\hat{B}^\alpha f(r)] \equiv (\chi_Q^0)^\alpha \int e^{iQ\cdot r} f(r)dr$ for an arbitrary real number α. Finally, the RDFs are written in the forms related to (2.15) and (2.16)

$$g_{II}(r) = \exp[-\beta v_{II}(r) + \Gamma_{II}(r) + B_{II}(r)] \tag{2.18}$$

$$g_{eI}(r) = n_e^0(r| v_{eI} - \Gamma_{eI}/\beta - B_{eI}/\beta)/n_0^e . \tag{2.19}$$

In practice we can think of the ion–electron mixture as a quasi-one-component fluid interacting via an effective interaction $v^{eff}(r)$. If this effective potential $v^{eff}(r)$ is defined in such a way that the ion–ion RDF $g_{II}(r)$ should be equal with the RDF $g(r)$ of the quasi-one-component fluid, the expression for $v^{eff}(Q)$ is shown to be in the Fourier transformed form:

$$\beta v^{eff}(Q) \equiv \beta v_{II}(Q) - \frac{|C_{eI}(Q)|^2 n_0^e \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0} \tag{2.20}$$

$$= \beta v_{II}(Q) - C_{eI}(Q)\rho(Q) \tag{2.21}$$

when the bridge function of one-component system is chosen to be $B_{II}(r)$ of the mixture.

All the above equations (2.1)–(2.21) are *exact* expressions, although formal ones, within the framework of the DF theory applied to the ion–electron mixture, provided that the ions are taken as *classical* particles and the ion–ion and electron–ion interactions are *binary*. It is worth pointing that the above equations express the following important facts:

(A) We can describe a liquid metal or a plasma *always* as a one-component fluid interacting via a *pairwise* potential (2.20) obtained by a *local* pseudopotential $-C_{eI}(Q)/\beta$ in the determination of the RDF $g_{II}(r)$, and need not introduce many-body forces, if the binary ion–ion interaction $v_{II}(r)$ is given beforehand in the ion-electron model. This can be seen by noting that the DF theory reduces the many-body problem to determine the ion-density distribution $n_0^I g_{II}(r)$ around a fixed ion in the coupled ion–electron mixture to the single-centre (one-body) problem to evaluate the non-interacting ion distribution under the effective one-centre external potential as (2.18) reveals. However, if we want to determine an ion–ion interaction $v_{II}(r)$, the many-centre (at least, two-centre) problem must be solved for the case where the overlap of core-electrons is significant, as will be discussed later.

(B) The conduction-electron distribution $n_0^e g_{eI}(r)$ around a fixed ion in the ion-electron mixture is *exactly* represented by the superposition of surrounding pseudoatoms, irrespective of the strength of an electron–ion interaction, as is shown by (2.14). Therefore, the conduction-electron distribution $\hat{n}_e(r)$ at arbitrary position r in the mixture may be described by the superposition of the pseudoatoms randomly distributed at $\{\hat{R}_i\}$ in such a way as $\hat{n}_e(r) = \sum_\alpha \rho(r - \hat{R}_\alpha)$. It should be remembered that (2.14) is based only on the premise that the ions constitute a classical fluid, and does not depend on the ion–ion interaction being binary. As a consequence, we can say that Ziman's neutral-pseudoatom model is *always* valid irrespective of the strength of an electron–ion interaction for any liquid metal where an ion–ion interaction becomes even a many-body force, provided that the system can be taken as an ion–electron mixture and the ions behave as classical particles.

In the ion–electron model where we know only the electron–electron interaction $v_{ee}(r)$ to be a pure Coulombic $v_{ee}^c(r) \equiv 1/r$, knowledge of many quantities is necessary for arriving at a set of closed integral equations for the RDF $g_{II}(r)$ from the above equations; the ionic charge Z_I, the electron–ion interaction $v_{eI}(r)$, the ion–ion interaction $v_{II}(r)$, the electron–electron DCF $C_{ee}(r)$, which is described by the local-field correction (LFC) $G(Q)$ in the form of $C_{ee}(Q) = -\beta v_{ee}^c(Q)(1 - G(Q))$, and two bridge functions $B_{iI}(r)$. In a liquid metal, (i) the LFC $G(Q)$ is surely replaced by that of the jellium model and (ii) the electron–ion bridge function can be neglected (this approximation is called the hypernetted-chain (HNC) approximation),

while (iii) the ion–ion bridge function $B_{II}(r)$ can be approximated by that of Percus -Yevick equation for the hard spheres in the spirit of the modified HNC equation [13]. In an attempt to get definite expressions for the electron–ion interaction $v_{eI}(r)$ and ionic charge Z_I from the atomic number Z_A, we viewed a liquid metal more fundamentally as a mixture of nuclei and electrons, and derived (iv) $v_{eI}(r)$ in the form

$$\tilde{v}_{eI}(r) \equiv -\frac{Z_A}{r} + \int v_{ee}^c(|r - r'|)\, n_e^b(r')\, dr' + \mu_{XC}(n_e^b(r) + n_0^e) - \mu_{XC}(n_0^e) \quad (2.22)$$

and (v) $Z_I = Z_A - \int n_e^b(r) dr$, which are determined in a self-consistent manner by coupling with the ion–electron model [6]; the RDF $n_0^e g_{eI}(r)$ and the bound-electron distribution $n_e^b(r)$ of a constituent ion are determined at the same time by solving the wave equation for an electron under the external potential $v_{eI}^{eff}(r)$ of (2.4). In the above, $\mu_{XC}(n_e(r))$ denotes the exchange-correlation potential and $v_{ij}^c(r)$ indicates a pure Coulombic potential between i–j particles. The DF theory applied to the nucleus–electron model remains the ion–ion interaction as undetermined. Therefore, we assume the ion–ion interaction $v_{II}(r)$ to be a pure Coulombic potential between ions: (vi) $v_{II}(r) = Z_I^2/r \equiv v_{II}^c(r)$. With the aid of these six approximations, we obtain a set of closed integral equations for RDF $g_{iI}(r)$ in a liquid metal with the atomic number Z_A as the only input: an application of these integral equations to a liquid metallic lithium [7] shows to give structure factors in good agreement with the experiment. However, the Coulombic approximation (vi) to $v_{II}(r)$ restricts its validity for a system where the ions are so small and rigid that the overlap of core-electrons is neglected. On the other hand, the definition (v) of Z_I is based on an implicit assumption that the bound-electrons are clearly distinct from the free-electrons: thus, a resonant state, which contains a strongly localized contribution, cannot be treated by this approximation. Hence, the applicability of this set of integral equations with six approximations is limited to 'simple metallic' system, where the overlap of core-electrons is small and no significant resonant state appears. It is, however, important to realise that this restriction does not comes from the ion–electron model, but is ascribed to the approximations introduced to obtain closed integral equations. Actually, we can treat 'non-simple metallic' system within the ion–electron model as will be shown later, if the definition of ionization Z_I is extended to involve a resonant state, and the ion–ion interaction $v_{II}(r)$ are determined by taking account of the core-electron overlap. In this respect, we notice that the overlap interaction between atoms or ions with the closed-shell electrons can be calculated by a simple but extremely useful method proposed by Gordon and Kim [9], which is summarised in the next subsection along with its variations.

2.2. The Gordon–Kim model and its generalization

According to the DF theory, the total energy of a system consisting of N nuclei with an atomic number Z_A and $Z_A N$ electrons is written in the adiabatic approximation in terms of the electron density distribution $\hat{n}_e(r)$ around nuclei fixed at $\{R_1 \cdots R_N\}$:

$$E_{tot}[\hat{n}_e | R_1 \cdots R_N] = T_s[\hat{n}_e] + E_{XC}[\hat{n}_e] + E_{es}[\hat{n}_e] \quad (2.23)$$

where the electrostatic energy of this system is given by

$$E_{es}[\hat{n}_e] \equiv \frac{1}{2} \int v_{ee}^c(|r - r'|)\hat{n}_e(r)\hat{n}_e(r')\, dr\, dr'$$
$$+ \sum_{\alpha=1}^{N} \int v_{eN}^c(|r - R_\alpha|)\hat{n}_e(r)\, dr + \frac{1}{2}\sum_{\alpha \neq \beta} \frac{Z_A^2}{R_{\alpha\beta}} \qquad (2.24)$$

and $T_s[\hat{n}_e]$ and $E_{XC}[\hat{n}_e]$ denote the kinetic and exchange-correlation energies, respectively, with $R_{\alpha\beta} \equiv R_\alpha - R_\beta$. The DF theory states that the electron density distribution $\hat{n}_e(r)$ can be obtained by solving the wave equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r|\hat{n}_e) \right] \phi_n(r) = \epsilon_n \phi_n(r) \qquad (2.25)$$

for an electron under the effective external potential:

$$v_{eff}(r|\hat{n}_e) \equiv -\frac{Z_A}{r} + \int v_{ee}^c(|r - r'|)\, dr' + \frac{\delta E_{XC}}{\delta \hat{n}_e(r)} - \mu_e^{int}\ . \qquad (2.26)$$

However, it is not so easy work to solve this multi-centre problem self-consistently. To circumvent this difficulty, Gordon and Kim [9] assumed that the electronic charge density $\hat{n}_e(r)$ can be approximated by a superposition of charge densities $\rho_a(r)$ of free atoms even for the overlap region of atoms:

$$\hat{n}_e(r) \approx n_e^f(r) \equiv \sum_{\alpha=1}^{N} \rho_a(r - R_\alpha) = \sum_\alpha \rho_a^{(\alpha)}(r)\ . \qquad (2.27)$$

Then, the total energy is written approximately in the form

$$E_{tot}[\hat{n}_e|R_1 \cdots R_N] \approx \Delta T_s[n_e^f] + \Delta E_{XC}[n_e^f] + \Delta E_{es} + N\epsilon_{atom} \qquad (2.28)$$

which comprises the total energy of N atoms with

$$\epsilon_{atom} = T_s[\rho_a] + E_{XC}[\rho_a] + \frac{1}{2} \int v_{ee}^c(|r - r'|)\rho_a(r)\rho_a(r')\, dr\, dr'$$
$$- \int \frac{Z_A}{r}\rho_a(r)\, dr \qquad (2.29)$$

and the difference of the kinetic, exchange-correlation and electrostatic energies from those of N atoms, as written respectively in the following

$$\Delta T_s[n_e^f] \equiv T_s[n_e^f] - \sum_{\alpha=1}^{N} T_s[\rho_a(r - R_\alpha)] \qquad (2.30)$$

$$\Delta E_{XC}[n_e^f] \equiv E_{XC}[n_e^f] - \sum_{\alpha=1}^{N} E_{XC}[\rho_a(r - R_\alpha)] \qquad (2.31)$$

$$\Delta E_{es} \equiv \frac{1}{2}\sum_{\alpha \neq \beta} \int \frac{Z_A(r)Z_A(r')}{|r - r' - R_{\alpha\beta}|}\, dr\, dr' \qquad (2.32)$$

with $Z_A(r) \equiv Z_A \delta(r) - \rho_a(r)$. Therefore, equation (2.28) applied to the two-nuclei system generates an interaction potential $v(r)$ between two closed-shell atoms in a free space as follows

$$v(|R_1 - R_2|) \approx \Delta T_s[n_e^f|R_1 R_2] + \Delta E_{XC}[n_e^f|R_1 R_2]$$
$$+ \int \frac{Z_A(r) Z_A(r')}{|r - r' - R_{12}|} \, dr \, dr' . \tag{2.33}$$

When we adopt the local-density approximation (LDA) to the kinetic energy T_s in addition to the exchange–correlation energy E_{XC}, the above equation was shown to give a simple but good evaluation of the atomic interaction [14].

In general, the LDA is not so a good approximation when applied to the kinetic-energy functional in contrast with the exchange–correlation energy, which can be fairly well described by the LDA. In this respect, Harris [10] extended the Gordon–Kim approach to allow a description of bonding in general, not restricted to inert atom interaction, by treating the kinetic energy in the Kohn–Sham manner [15] rather than in the LDA. Exactly to obtain the kinetic-energy $T_s[\hat{n}_e]$, the wave equation (2.25) need to be solved self-consistently: that is, the self-consistent potential $v^{\text{eff}}(r|\hat{n}_e)$ is required for the wave equation (2.25), which is solved iteratively to achieve self-consistency. In the Harris approach, this self-consistent potential is approximated by $\widetilde{V}_{\text{eff}}(r) \equiv v_{\text{eff}}(r|n_e^f)$, where the total electron density distribution $\hat{n}_e(r)$ is replaced by $n_e^f(r)$, the superposition of electron-densities of isolated atoms as was done in (2.27) of the Gordon–Kim scheme; then, the approximated self-consistent Hamiltonian $\widetilde{H}$ is written as

$$\widetilde{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + \widetilde{V}_{\text{eff}}(r) = \sum_n |n\rangle \tilde{\epsilon}_n \langle n| \tag{2.34}$$

with $\widetilde{H}|n\rangle = \tilde{\epsilon}_n |n\rangle$. In this way, the expression for the change in the kinetic energy as the atoms are condensed to form a liquid, is derived as

$$\Delta T_s = \sum_n f(\tilde{\epsilon}_n)\tilde{\epsilon}_n - \sum_{\alpha=1}^{N} \sum_\ell f(\epsilon_\ell^{(\alpha)})\epsilon_\ell^{(\alpha)}$$
$$- \sum_{\alpha=1}^{N} \int \rho_a^{(\alpha)}(r)[\widetilde{V}_{\text{eff}}(r) - V_{\text{eff}}^{(\alpha)}(r)] \, dr \tag{2.35}$$

$$= \text{Tr}(\tilde{n}_e^{\text{out}} - n_e^f)\widetilde{H} \tag{2.36}$$

with the definitions: $\tilde{n}_e^{\text{out}} \equiv \sum_n f(\tilde{\epsilon}_n)|n\rangle\langle n|$ and

$$\text{Tr}(\tilde{n}_e^{\text{out}}\widetilde{H}) \equiv \sum_n \langle n|\tilde{n}_e^{\text{out}}\widetilde{H}|n\rangle = \sum_n f(\tilde{\epsilon}_n)\tilde{\epsilon}_n . \tag{2.37}$$

Here, $\epsilon_\ell^{(\alpha)}$ denotes the energy level associated with single-centre potential of α-site and $f(\epsilon) \equiv 1/[\exp(\beta(\epsilon - \mu_e^0)) + 1]$. On the basis of the equation (2.36), Sutton *et al* [16] have presented the tight-binding bond (TBB) model [16, 17] of cohesion

and interatomic forces; there, the kinetic energy term is described by tight-binding approximation with use of atomic orbital functions.

There are several problems to be investigated concerning the Gordon–Kim method and the Harris extension. (i) This method does not take account of the presence of free electrons which can not be approximated by the tight-binding approximation; therefore, the core–core interaction in a liquid metal or a plasma can not be treated by this method. (ii) The superposition of electron densities of isolated atoms may not be good approximation for a high-density plasma or a liquid metal, where the free electrons plays an important role in the determination of electronic structure. (iii) Then, other than atomic electron densities, what electron density $\rho^T(r)$ can we use to superimpose in a better representation of real electron density $\hat{n}_e(r)$ under the external potential caused by many fixed nuclei by the form: $n_e^I(r) = \sum_{\alpha=1}^{N} \rho^T(r - R_\alpha)$? (iv) How can we obtain self-consistent base functions in the tight-binding approximation applied to (2.36), especially for a plasma?

3. Formulation

3.1. The single-centre problem

A liquid metal or a plasma can be more fundamentally considered as a nucleus–electron mixture consisting of N_I nuclei of charge Z_A and $Z_A N_I$ electrons. Here, we single out one nucleus and fix it at the origin; then, fixing a nucleus in the mixture induces an inhomogeneous system under the external potentials caused by the fixed nucleus at the origin. This model can be equivalently translated into a simpler system; an inhomogeneous coupled ion–electron mixture, which consists of $(N_I - 1)$ ions interacting via a potential $v_{II}(r)$ and $Z_I(N_I-1)+Z_A$ electrons, with one fixed nucleus at the origin. Here, the ionic structure and its ionic charge Z_I are to be determined in a self-consistent manner. Hence, the nucleus- and electron-density distributions in the nucleus–electron mixture with a fixed nucleus at the origin become identical with the ion- and electron-density distributions, $n_i(r|N)$, in the inhomogeneous ion–electron mixture in the presence of external potentials, $U_I(r) = v_{IN}(r)$ and $U_e(r) = v_{eN}^c(r)$, for ions and electrons caused by the fixed nucleus at the origin, where $v_{IN}(r)$ is unknown at this stage although the electron–nucleus interaction $v_{eN}^c(r)$ is surely a pure Coulombic $-Z_A/r$. As a consequence the DF theory can be applied to this system by taking as a reference system [1] a mixture composed of $(N_I - 1)$ non-interacting ions and $Z_I(N_I - 1) + Z_A$ non-interacting electrons; each ion is assumed to have Z_B bound-electrons with a distribution $\rho_b(r)$. Hereafter, this reference system will be referred to as the average-ion model, of which intrinsic free energy is represented by

$$\mathcal{F}_0 = \frac{1}{\beta} \int n_I(r|N) \ln[n_I(r|N)\lambda^3] \, dr + (N_I - 1) f_e^b[\rho_b] + \mathcal{F}_0^e[n_e(r|N)] \tag{3.1}$$

where $f_e^b[\rho_b]$ denotes the free-energy of bound electrons in an ion, $\mathcal{F}_0^e[n_e(r|N)]$ is the intrinsic free-energy of non-interacting electrons, and λ indicates the thermal wavelength of ion. Therefore, the thermodynamic potential Ω of the system is written in the light of the average-ion model as

$$\Omega = \mathcal{F}_0 + \mathcal{F}_{\text{int}} - \int [\mu_e - v_{eN}^c(r)] n_e(r|N) \, dr - \int [\mu_I - v_{IN}(r)] n_I(r|N) \, dr \tag{3.2}$$

with the interaction part of the intrinsic free-energy $\mathcal{F}_{\text{int}} \equiv \mathcal{F} - \mathcal{F}_0$, that is the difference of the intrinsic free energy between real and non-interacting systems. The DF theory afford to give the exact expressions for ion- and electron-density distributions

$$n_{\text{I}}(r|N) = n_0^{\text{I}} \exp[-\beta v_{\text{IN}}^{\text{eff}}(r)] \tag{3.3}$$

$$n_{\text{e}}(r|N) = n_{\text{e}}^0(r|v_{\text{eN}}^{\text{eff}}) = n_{\text{e}}^{\text{b}}(r|N) + n_{\text{e}}^{\text{c}}(r|N) \tag{3.4}$$

with effective external potentials ($i =$ I or e) defined in terms of $\mathcal{F}^{\text{int}}$ as follows:

$$v_{i\text{N}}^{\text{eff}}(r) = v_{i\text{N}}(r) + \frac{\delta \mathcal{F}_{\text{int}}}{\delta n_i(r)} - \mu_i^{\text{int}} . \tag{3.5}$$

Here, n_{e}^{b} and n_{e}^{c} denote the bound- and conduction-electron distributions around the fixed nucleus, respectively. If we sit on the nucleus fixed at the origin, we can see a world where some bound electrons go round it and the free electrons are accumulated as described by (3.4), and the ions are pushed away from it according to (3.3). Since we can see the same world viewed from the nucleus fixed at the origin even if we sit on any ion in the reference system, the bound electrons around the nucleus at the origin should be taken to constitute an ion around the origin, which is the same density distribution $\rho_{\text{b}}(r)$ of the reference ion in the premise; thus, we obtain a self-consistent condition to determine $\rho_{\text{b}}(r)$ and Z_{B}:

$$\rho_{\text{b}}(r) = n_{\text{e}}^{\text{b}}(r|N) \tag{3.6}$$

and hence $Z_{\text{B}} \equiv \int n_{\text{e}}^{\text{b}}(r|N) \, dr$. At this stage, however, we does not describe a criterion to discriminate between bound and conduction states: 'bound' states will be defined later. From the above fact, we can take the interaction $v_{\text{IN}}(r)$ between the central nucleus and a surrounding ion to be identical with the interaction $v_{\text{II}}(r)$ between two ions: $v_{\text{IN}}(r) = v_{\text{II}}(r)$, since the central nucleus has the same bound electrons forming an ion to that of other ion in the reference system. For the purpose of obtaining a tractable formula for $v_{\text{eN}}^{\text{eff}}(r)$, we approximate the chemical potential involved in (3.5) in the form (for a detail derivation, see [6]):

$$\frac{\delta \mathcal{F}_{\text{int}}}{\delta n_{\text{e}}(r)} - \mu_{\text{e}}^{\text{int}} \approx \int v_{\text{ee}}^{\text{c}}(|r - r'|) \, n_{\text{e}}^{\text{b}}(r') \, dr' + \mu_{\text{XC}}(n_{\text{e}}^{\text{b}}(r) + n_0^{\text{e}}) - \mu_{\text{XC}}(n_0^{\text{e}})$$

$$+ \int \frac{C_{\text{ee}}(|r - r'|)}{-\beta} \delta n_{\text{e}}^{\text{c}}(r'|N) \, dr' + \int \frac{C_{\text{eI}}(|r - r'|)}{-\beta} \delta n_{\text{I}}(r'|N) \, dr' \tag{3.7}$$

in terms of the DCFs defined by (2.5). Henceforth, the effective electron-nucleus interaction is obtained as

$$v_{\text{eN}}^{\text{eff}}(r) = \tilde{v}_{\text{eI}}(r) + \int \frac{C_{\text{ee}}(|r - r'|)}{-\beta} \delta n_{\text{e}}^{\text{c}}(r'|N) \, dr'$$

$$+ \int \frac{C_{\text{eI}}(|r - r'|)}{-\beta} \delta n_{\text{I}}(r'|N) \, dr' \tag{3.8}$$

$$= v_{\text{eI}}^{\text{eff}}(r) \tag{3.9}$$

which is identical with the electron–ion interaction $v_{eI}^{eff}(r)$ of (2.4) with the bare electron–ion interaction $\tilde{v}_{eI}(r)$ given before by (2.22). On the other hand, the effective ion-nucleus interaction $v_{IN}^{eff}(r)$ is now considered to be equal with $v_{II}^{eff}(r)$

$$
\begin{aligned}
v_{IN}^{eff}(r) &= v_{II}(r) + \int \frac{C_{Ie}(|r - r'|)}{-\beta} \delta n_e^c(r'|N) \, dr' \\
&\quad + \int \frac{C_{II}(|r - r'|)}{-\beta} \delta n_I(r'|N) \, dr' - B_{II}(r)/\beta \\
&\equiv v_{II}^{eff}(r)
\end{aligned}
\tag{3.10}
$$

as is shown by (2.4) in the ion–electron model because of $v_{IN}(r) = v_{II}(r)$. Hence, the above equations, (3.8) and (3.11), show that the nucleus–electron model with the average-ion reference leads to the ion–electron model, where the electron–ion interaction (2.22) and the bound-electron distribution $\rho_b(r)$ are given in a self-consistent manner.

The electron–ion RDF $g_{eI}(r)$ should be identified with the conduction electron distribution $n_e^c(r|N)/n_0^e$, since the bound electron part $n_e^b(r|N)$ constitutes an ion; thus, in the nucleus–electron model there follows the similar relation to (2.11):

$$
S_{eI}(Q) = \sqrt{n_0^e n_0^I} \mathcal{F}_Q[n_e^c(r|N)/n_0^e - 1] = \frac{\rho_c(Q)}{\sqrt{Z_I}} S_{II}(Q)
\tag{3.11}
$$

with

$$
\rho_c(Q) \equiv \frac{n_0^e C_{eI}(Q) \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0} \, .
\tag{3.12}
$$

It should be noted that the bare ion–ion interaction $v_{II}(r)$ remains an undetermined quantity in the nucleus–electron model. To achieve an expression determining $v_{II}(r)$, we have to couple the above results with a multi-center problem as will be mentioned in the next subsection. In this respect, it should be kept in mind that the nucleus–electron model provides the total electron distribution, including the bound electrons, around the fixed nucleus in the form:

$$
n^T(r|N) = n_e(r|N) + n_0^I \int \rho_b(r - r') g_{II}(r') \, dr'
\tag{3.13}
$$

$$
= \rho_{pa}(r) + n_0^I \int \rho_{pa}(r - r') g_{II}(r') \, dr'
\tag{3.14}
$$

as is seen from (3.11). This relation suggests that the electron distribution under the external potential caused by the nuclei randomly distributed at $\{R_\alpha\}$ may be represented by a superposition of neutral pseudoatoms with a distribution

$$
\rho_{pa}(r) \equiv \rho_b(r) + \rho_c(r)
\tag{3.15}
$$

in the form

$$
n_e^f(r) = \sum_\alpha \rho_{pa}(r - R_\alpha) = \hat{n}_b^f(r) + \hat{n}_e^c(r) \, .
\tag{3.16}
$$

Here,

$$\hat{n}_b^f(r) \equiv \sum_\alpha \rho_b(r - R_\alpha) = \sum_\alpha \rho_b^{(\alpha)}(r) = \int \rho_b(r - r')\hat{n}_I(r')\,dr' \tag{3.17}$$

$$\hat{n}_c^c(r) \equiv \int \rho_c(r - r')\hat{n}_I(r')\,dr' \tag{3.18}$$

where $\hat{n}_I(r)$ denotes the microscopic nuclear distribution: $\hat{n}_I(r) \equiv \sum_{\alpha=1}^{N_I} \delta(r - R_\alpha)$. This approximation forms the starting point for a study of the multi-centre problem to determine the electronic structure and the thermodynamic properties of the system in the presence of randomly distributed nuclei at $\{R_1 \cdots R_N\}$.

3.2. The multi-centre problem

As was discussed in the previous subsection, we consider an interacting system of N nuclei and $Z_A N$ electrons forming a liquid metal contained in a volume V at temperature $T = 1/k_B\beta$: the Hamiltonian of the system is written as

$$\hat{H} = \hat{H}_{NN} + \hat{H}_{ee} + \hat{H}_{eN} \tag{3.19}$$

where

$$\hat{H}_{NN} \equiv \sum_{\alpha=1}^N \frac{\hat{P}_\alpha^2}{2M} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_A^2}{|\hat{R}_\alpha - \hat{R}_\beta|} \tag{3.20}$$

$$\hat{H}_{ee} \equiv \sum_{i=1}^{Z_A N} \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\hat{r}_i - \hat{r}_j|} \tag{3.21}$$

$$\hat{H}_{eN} \equiv -\sum_{i,\alpha} \frac{Z_A}{|\hat{r}_i - \hat{R}_\alpha|} \tag{3.22}$$

In the above equations, $\hat{R}_\alpha$ and $\hat{P}_\alpha$ denote nuclear coordinates and momenta, and $\hat{r}_i$ and $\hat{p}_i$ refer to the electrons with the nuclear and electron masses, M and m, respectively. Since the nuclei behave as classical particles, we can consider their co-ordinates and momenta to be commutable: $[\hat{R}_\alpha, \hat{P}_\alpha] = 0$. As a result, the canonical partition function of the system can be written in a factorised form:

$$Z_N \equiv \text{Tr}\exp(-\beta\hat{H}) = \text{Tr}[\exp(-\beta\hat{H}_{NN})\exp(-\beta(\hat{H}_{ee} + \hat{H}_{eN}))] \tag{3.23}$$

which reduces to the canonical partition function for a classical one-component fluid:

$$Z_N = \frac{1}{N!h^{3N}} \int dR_1\,dR_2 \cdots dR_N\,dP_1\,dP_2 \cdots dP_N \exp(-\beta H_{\text{eff}}) \tag{3.24}$$

with an effective Hamiltonian for interacting N classical particles

$$H_{\text{eff}} = \hat{H}_{NN} + F_e(R_1 \cdots R_N) \tag{3.25}$$

where F_e is defined by

$$\exp[-\beta F_e(\mathbf{R}_1 \cdots \mathbf{R}_N)] \equiv \text{Tr}_e \exp(-\beta(\hat{H}_{ee} + \hat{H}_{eN})) \tag{3.26}$$

and plays a role of a many-body interaction among particles. Since F_e is essentially the free-energy of the electrons under the external potential caused by nuclei fixed at $\{\mathbf{R}_\alpha\}$, it can be represented in terms of the electron density $\hat{n}_e(r)$ on the basis of the DF theory:

$$F_e(\mathbf{R}_1 \cdots \mathbf{R}_N) = F_e[\hat{n}_e | \mathbf{R}_1 \cdots \mathbf{R}_N] = F_e[\hat{n}_e, \hat{n}_I]$$
$$= F_0[\hat{n}_e] + F_{XC}[\hat{n}_e, \hat{n}_I] + \frac{1}{2} \int v_{ee}^c(|r - r'|) \hat{n}_e(r) \hat{n}_e(r') \, dr \, dr'$$
$$+ \sum_\alpha \int \hat{n}_e(r) v_{eN}^c(|r - \mathbf{R}_\alpha|) \, dr . \tag{3.27}$$

Thus, the effective Hamiltonian H_{eff} can be rewritten as

$$H_{\text{eff}} = \sum_{\alpha=1}^N \frac{P_\alpha^2}{2M} + F_0[\hat{n}_e] + F_{XC}[\hat{n}_e, \hat{n}_I] + E_{es}[\hat{n}_e] . \tag{3.28}$$

Here, the electrostatic energy E_{es} is defined by (2.24).

We are now in a position to rewrite the effective Hamiltonian (3.28) in a tractable form on the basis of the superposition approximation (3.16). In the first place, the electrostatic energy E_{es} of (2.24) is shown to be rewritten after some tedious calculation in the form representing the conduction-electron and bound electron contributions explicitly

$$E_{es}[\hat{n}_e] = \frac{1}{2} \int \frac{\delta \hat{n}_e^c(r) \delta \hat{n}_e^c(r')}{|r - r'|} \, dr \, dr' + \int \bar{v}_{eI}(|r - r'|) \delta \hat{n}_e^c(r) \delta \hat{n}_I(r') \, dr \, dr'$$
$$+ \int \frac{Z_I^2}{|r - r'|} (n_0^I)^2 [\hat{g}_{II}(r - r') - 1] \, dr \, dr'$$
$$+ N \left[-\int \frac{Z_A}{r} \rho_b(r) dr + \frac{1}{2} \int \frac{\rho_b(r) \rho_b(r')}{|r - r'|} \, dr \, dr' \right.$$
$$\left. - n_0^e \frac{2\pi}{3} \int \rho_b(r) r^2 dr \right]$$
$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \left[\int \frac{Z_I(r) Z_I(r')}{|r - r' + \mathbf{R}_{\alpha\beta}|} \, dr \, dr' - \frac{Z_I^2}{R_{\alpha\beta}} \right] \tag{3.29}$$

with $Z_I(r) \equiv Z_A \delta(r) - \rho_b(r)$ and

$$\bar{v}_{eI}(r) \equiv -\frac{Z_A}{r} + \int v_{ee}^c(|r - r'|) \rho_b(r') \, dr' . \tag{3.30}$$

In the above equation, $\delta \hat{n}_e^c(r) \equiv \hat{n}_e^c(r) - n_0^e$ and $\delta \hat{n}_I(r) \equiv \hat{n}_I(r) - n_0^I$ denote the deviations of the conduction-electron distribution and random ion-distribution from their uniform densities, respectively, and

$$(n_0^I)^2 [\hat{g}_{II}(r - r') - 1] \equiv \delta \hat{n}_I(r) \delta \hat{n}_I(r') - \sum_\alpha \delta(r - \mathbf{R}_\alpha) \delta(r' - \mathbf{R}_\alpha) \tag{3.31}$$

the configurational average of which generates the RDF $(n_0^I)^2[g_{II}(|r - r'|) - 1]$. The above expression (3.29) for the electrostatic energy can be obtained from (2.24) by adding and subtracting a neutralising background $n_+(r) = \sum_\alpha \rho_b(r - R_\alpha)$ at the first time, and secondly the neutralising uniform positive background n_0^e, and the following relation is used in the derivation of (3.29):

$$\sum_\alpha \int \left[\bar{v}_{eI}(|r - R_\alpha|) + \frac{Z_I}{|r - R_\alpha|}\right] n_0^e \, dr = N n_0^e \int \left(\bar{v}_{eI}(r) + \frac{Z_I}{r}\right) dr$$

$$= n_0^e \int dr \left[\int dr' \frac{\hat{n}_b^f(r')}{|r - r'|} + \sum_\alpha \frac{-Z_B}{|r - R_\alpha|}\right]$$

$$= - N n_0^e \frac{2\pi}{3} \int \rho_b(r) r^2 dr \,. \tag{3.32}$$

On the other hand, the exchange–correlation part of free-energy of electrons is assumed to be divided into the three parts: the bound electron and conduction-electron terms and their coupled term, as described by

$$F_{XC}[\hat{n}_e] = F_{XC}[\hat{n}_e | R_1 \cdots R_N] = F_{XC}[\hat{n}_e, \hat{n}_I]$$

$$\approx F_{XC}[\hat{n}_e^b] + \sum_\alpha \int \bar{\mu}_{XC}(|r - R_\alpha|)\hat{n}_e^c(r) \, dr + F_{XC}[\hat{n}_e^c, \hat{n}_I] \tag{3.33}$$

with

$$\bar{\mu}_{XC}(r) \boxminus \mu_{XC}(\rho_b(r) + n_0^e) - \mu_{XC}(n_0^e) \,. \tag{3.34}$$

The conduction-electron part of F_{XC} is approximated by the functional-expansion around uniform densities to the second order:

$$F_{XC}[\hat{n}_e^c, \hat{n}_I] \approx F_{XC}[n_0^e] + \frac{1}{2} \int \left.\frac{\delta^2 F_{XC}}{\delta \hat{n}_e^c(r)\delta \hat{n}_e^c(r')}\right|_0 \delta \hat{n}_e^c(r)\delta \hat{n}_e^c(r') \, dr \, dr'$$

$$+ \int \left.\frac{\delta^2 F_{XC}}{\delta \hat{n}_e^c(r)\delta \hat{n}_I(r')}\right|_0 \delta \hat{n}_e^c(r)\delta \hat{n}_I(r') \, dr \, dr' \tag{3.35}$$

$$\approx F_{XC}[n_0^e] + \frac{1}{2} \int \frac{C_{ee}^{XC}(|r - r'|)}{-\beta} \delta \hat{n}_e^c(r)\delta \hat{n}_e^c(r') \, dr \, dr'$$

$$+ \int \frac{C_{eI}^{XC}(|r - r'|)}{-\beta} \delta \hat{n}_e^c(r)\delta \hat{n}_I(r') \, dr \, dr' \,. \tag{3.36}$$

In the above, we introduce a further approximation by the following replacement to associate with the DCFs $C_{ij}(r) \equiv C_{ij}^{XC}(r) - \beta v_{ij}(r)$

$$\left.\frac{\delta^2 F_{XC}}{\delta \hat{n}_i(r)\delta \hat{n}_j(r')}\right|_0 \approx \left.\frac{\delta^2 \mathcal{F}_{XC}}{\delta \hat{n}_i(r)\delta \hat{n}_j(r')}\right|_0 = - C_{ij}^{XC}(|r - r'|)/\beta \tag{3.37}$$

which implies that the functional-derivative of F_{XC} of the electrons in the presence of randomly distributed nuclei is replaced by that of the exchange–correlation free-energy of the ion–electron mixture. Here, the electron-density functional

$F_{\mathrm{XC}}[\hat{n}_e|R_1\cdots R_N]$ of one-component system is thought of as the two-component functional of the electron-density $\hat{n}_e(r)$ and the random ion distribution $\hat{n}_I(r)$, since the nucleus number N is so large that we can treat the nuclear distribution $\hat{n}_I(r)$ statistically. Also the conduction-electron part of $F_0[\hat{n}_e] = F_0[\hat{n}_e^b] + F_0[\hat{n}_e^c]$ in (3.28) is approximated by the functional-expansion around uniform densities to the second order:

$$F_0[\hat{n}_e^c] \approx F_0[n_0^c] + \frac{1}{2}\int \left.\frac{\delta^2 F_0}{\delta\hat{n}_e^c(r)\delta\hat{n}_e^c(r')}\right|_0 \delta\hat{n}_e^c(r)\delta\hat{n}_e^c(r')\,\mathrm{d}r\,\mathrm{d}r' \tag{3.38}$$

$$= F_0[n_0^c] + \frac{1}{2\beta}\int C_{ee}(|r-r'|)\delta\hat{n}_e^c(r)\delta\hat{n}_e^c(r')\,\mathrm{d}r\,\mathrm{d}r'$$

$$+ \frac{1}{2\beta}\int C_{eI}(|r-r'|)\delta\hat{n}_e^c(r)\delta\hat{n}_I(r')\,\mathrm{d}r\,\mathrm{d}r' \ . \tag{3.39}$$

In the above derivation of (3.39), the superposition approximation (3.18) with neutral pseudoatoms (3.12) is used in conjunction with the relation

$$\mathcal{F}_Q\left[\left.\frac{\delta^2 F_0[\hat{n}_e^c]}{\delta\hat{n}_e^c(r)\delta\hat{n}_e^c(r')}\right|_0\right] = \frac{1}{n_0^e\beta\chi_Q^0} \ . \tag{3.40}$$

Consequently, by the combined use of (3.39), (3.29) and (3.33) with (3.36), the effective Hamiltonian (3.28) can be altered to read

$$H_{\mathrm{eff}} = \Delta T_s[\hat{n}_b^f] + \Delta E_{\mathrm{XC}}[\hat{n}_b^f] + \frac{1}{2}\sum_{\alpha\neq\beta}\left[\int\frac{Z_I(r)Z_I(r')}{|r-r'+R_{\alpha\beta}|}\,\mathrm{d}r\,\mathrm{d}r' - \frac{Z_I^2}{R_{\alpha\beta}}\right]$$

$$+ \int\frac{Z_I^2}{|r-r'|}(n_0^I)^2[\hat{g}_{II}(r-r')-1]\,\mathrm{d}r\,\mathrm{d}r'$$

$$+ \frac{1}{2\beta}\int C_{eI}(|r-r'|)\delta\hat{n}_e^c(r)\delta\hat{n}_I(r')\,\mathrm{d}r\,\mathrm{d}r'$$

$$+ \sum_{\alpha}\frac{P_\alpha^2}{2M} + F_0[n_0^c] + F_{\mathrm{XC}}[n_0^c] + N\epsilon_{\mathrm{ion}}$$

$$+ Nn_0^e\tilde{v}_{eI}^R(Q=0) \tag{3.41}$$

where

$$\Delta T_s[\hat{n}_b^f] \equiv T_s[\hat{n}_b^f] - \sum_{\alpha=1}^N T_s[\rho_b(r-R_\alpha)] \tag{3.42}$$

$$\Delta E_{\mathrm{XC}}[\hat{n}_b^f] \equiv E_{\mathrm{XC}}[\hat{n}_b^f] - \sum_{\alpha=1}^N E_{\mathrm{XC}}[\rho_b(r-R_\alpha)] \tag{3.43}$$

$$\epsilon_{\mathrm{ion}} \equiv T_s[\rho_b] + E_{\mathrm{XC}}[\rho_b] + \frac{1}{2}\int v_{ee}^c(|r-r'|)\rho_b(r)\rho_b(r')\,\mathrm{d}r\,\mathrm{d}r' - \int\frac{Z_A}{r}\rho_b(r)\,\mathrm{d}r \tag{3.44}$$

and

$$\tilde{v}_{\rm eI}^{R}(Q=0) \equiv \int \left(\tilde{v}_{\rm eI}(r) + \frac{Z_{\rm I}}{r}\right)\,{\rm d}\boldsymbol{r} = -\frac{2\pi}{3}\int \rho_{\rm b}(r)r^2{\rm d}\boldsymbol{r} + \int \tilde{\mu}_{\rm XC}(r)\,{\rm d}\boldsymbol{r} \ . \quad (3.45)$$

In the above, we made the following approximations:

$$F_0[\hat{n}_{\rm e}^{\rm b}] \approx T_{\rm s}[\hat{n}_{\rm e}^{\rm b}] \ , \quad F_{\rm XC}[\hat{n}_{\rm e}^{\rm b}] \approx E_{\rm XC}[\hat{n}_{\rm e}^{\rm b}] \quad (3.46)$$

since the electron density is so high in the core-region that the temperature effect can be ignored. Furthermore, this effective Hamiltonian is rewritten in a simple form

$$H_{\rm eff} = \sum_{\alpha=1}^{N}\frac{\boldsymbol{P}_\alpha^2}{2M} + \frac{1}{2}\sum_{\alpha\neq\beta}\left[\frac{Z_{\rm I}^2}{R_{\alpha\beta}} + v_{\rm ind}(R_{\alpha\beta})\right] + F' + \Delta T_{\rm s}[\hat{n}_{\rm b}^f] + \Delta E_{\rm XC}[\hat{n}_{\rm b}^f]$$
$$+ \frac{1}{2}\sum_{\alpha\neq\beta}\left[\int\frac{Z_{\rm I}(\boldsymbol{r})Z_{\rm I}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'+\boldsymbol{R}_{\alpha\beta}|}\,{\rm d}\boldsymbol{r}\,{\rm d}\boldsymbol{r}' - \frac{Z_{\rm I}^2}{R_{\alpha\beta}}\right] \quad (3.47)$$

where

$$F'/N \equiv \tfrac{1}{2}v_{\rm ind}(r=0) - \tfrac{1}{2}n_0^{\rm I}\lim_{Q\to 0}\left(\frac{4\pi Z_{\rm I}^2}{Q^2} + v_{\rm ind}(Q)\right)$$
$$+ F_0[n_0^{\rm e}]/N + F_{\rm XC}[n_0^{\rm e}]/N + \epsilon_{\rm ion} + n_0^{\rm e}\tilde{v}_{\rm eI}^R(Q=0) + \tfrac{3}{2}k_{\rm B}T \quad (3.48)$$

with

$$v_{\rm ind}(Q) \equiv -\frac{|C_{\rm eI}(Q)/\beta|^2 n_0^{\rm e}\beta\chi_Q^0}{1 - n_0^{\rm e}C_{\rm ee}(Q)\chi_Q^0} \ . \quad (3.49)$$

Finally, if the core-overlap interaction can be represented as a sum of a binary interaction

$$\Delta T_{\rm s}[\hat{n}_{\rm b}^f] + \Delta E_{\rm XC}[\hat{n}_{\rm b}^f] + \frac{1}{2}\sum_{\alpha\neq\beta}\left[\int\frac{Z_{\rm I}(\boldsymbol{r})Z_{\rm I}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'+\boldsymbol{R}_{\alpha\beta}|}\,{\rm d}\boldsymbol{r}\,{\rm d}\boldsymbol{r}' - \frac{Z_{\rm I}^2}{R_{\alpha\beta}}\right]$$
$$\approx \frac{1}{2}\sum_{\alpha\neq\beta}v_{\rm ol}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|)$$

$$(3.50)$$

the effective Hamiltonian (3.28) for a classical quasi-one-component fluid is written in the form

$$H_{\rm eff} = \sum_{\alpha=1}^{N}\frac{\boldsymbol{P}_\alpha^2}{2M} + \frac{1}{2}\sum_{\alpha\neq\beta}v^{\rm eff}(|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|) + F' \quad (3.51)$$

in terms of the effective ion–ion interaction defined by

$$\beta v^{\rm eff}(Q) \equiv \beta\tilde{v}_{\rm II}(Q) - \frac{|C_{\rm eI}(Q)|^2 n_0^{\rm e}\chi_Q^0}{1 - n_0^{\rm e}C_{\rm ee}(Q)\chi_Q^0} \quad (3.52)$$

with

$$\tilde{v}_{\mathrm{II}}(r) \equiv \frac{Z_{\mathrm{I}}^2}{r} + v_{\mathrm{ol}}(r) \ . \tag{3.53}$$

It is important to realise that this effective interaction is in essence the same to (2.20) given by the previous single-centre formulation except that the bare ion–ion interaction $\tilde{v}_{\mathrm{II}}(r)$ is now generated by the use of (3.50). Also we stress here that the equation (3.50) gives rise to an extension of the GK method to determine the ion–ion overlap interaction in the presence of conduction electrons. Now, for example, the internal energy of a liquid metal, where the conduction electrons are assumed to be perfectly degenerate, is given by

$$E = \langle H_{\mathrm{eff}} \rangle = \tfrac{1}{2} N n_0^{\mathrm{I}} \int v^{\mathrm{eff}}(r)[g_{\mathrm{II}}(r) - 1] \, \mathrm{d}r + \tfrac{1}{2} N v_{\mathrm{ind}}(r = 0) + \tfrac{1}{2} N n_0^{\mathrm{I}} v_{\mathrm{ol}}(Q = 0)$$

$$+ N n_0^{\mathrm{e}} \tilde{v}_{\mathrm{eI}}^R(Q = 0) + T_{\mathrm{s}}[n_0^{\mathrm{e}}] + E_{\mathrm{XC}}[n_0^{\mathrm{e}}]$$

$$+ \tfrac{3}{2} k_{\mathrm{B}} T N + N \epsilon_{\mathrm{ion}} \tag{3.54}$$

This expression is an extension of a formula for the internal energy derived previously [18] to the case of a liquid metal with core electrons.

At this point, let us apply the Harris formulation [10] to evaluate the core-overlap interaction by (3.50) without use of the LDA to T_{s}. As a first step, the effective external potential $v_{\mathrm{eff}}(r|\hat{n}_e)$ in the DF theory is expressed in the form avoiding an iteration process to set up a self-consistent potential

$$v_{\mathrm{eff}}(r|\hat{n}_e) \approx v_{\mathrm{eff}}(r|n_e^f) \equiv \widetilde{V}_{\mathrm{eff}}^{(\mathrm{M})}(r|R_1 \cdots R_N) \tag{3.55}$$

by means of the superposition approximation (3.16). Thus, a new output of bound electron density $\hat{n}_{\mathrm{b}}^{\mathrm{out}}(r)$ is obtained as

$$\hat{n}_{\mathrm{b}}^{\mathrm{out}}(r) \equiv \sum_{n \in \mathrm{bound}} f(\tilde{\epsilon}_n) |\varphi_n(r)|^2 \tag{3.56}$$

by solving the wave equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \widetilde{V}_{\mathrm{eff}}^{(\mathrm{M})}(r|R_1 \cdots R_N) \right] \varphi_n(r) \equiv \widetilde{H} \varphi_n(r) = \tilde{\epsilon}_n \varphi_n(r) \ . \tag{3.57}$$

Consequently, the kinetic-energy difference $\Delta T_{\mathrm{s}}[\hat{n}_{\mathrm{b}}^f]$ is expressed with the aid of (3.56) in terms of new energy levels $\tilde{\epsilon}_i$ in the form

$$\Delta T_s[\hat{n}_{\mathrm{b}}^f] = \sum_{n \in \mathrm{bound}} f(\tilde{\epsilon}_n) \tilde{\epsilon}_n - \sum_{\alpha=1}^N \sum_{n \in \mathrm{bound}} f(\epsilon_n^{(\alpha)}) \epsilon_n^{(\alpha)}$$

$$- \sum_{\alpha=1}^N \int \rho_{\mathrm{b}}^{(\alpha)}(r) [\widetilde{V}_{\mathrm{eff}}^{(\mathrm{M})}(r) - V_{\mathrm{eff}}^{(\mathrm{S})}(r|\alpha)] \, \mathrm{d}r \tag{3.58}$$

$$= \mathrm{Tr}(\hat{n}_{\mathrm{b}}^{\mathrm{out}} - \hat{n}_{\mathrm{b}}^f) \widetilde{H} \tag{3.59}$$

where $V_{\text{eff}}^{(S)}(r|\alpha)$ is a single-centre potential at α-site as discussed in section 3.1 and $\widetilde{V}_{\text{eff}}^{(M)}(r)$ is a multi-centre potential which is assumed now to be given by the superposition of the muffin-tin potential without overlap, as described respectively by

$$V_{\text{eff}}^{(S)}(r|\alpha) \equiv v_{\text{eN}}^{\text{eff}}(|r - R_\alpha|) \tag{3.60}$$

$$\widetilde{V}_{\text{eff}}^{(M)}(r) = \sum_{\alpha=1}^{N} v_{\text{MT}}(|r - R_\alpha|) . \tag{3.61}$$

At this stage, if we determine the muffin-tin potential $v_{\text{MT}}(r)$ to fulfill the condition that $\delta\langle\Omega_e\rangle/\delta\rho_{\text{pa}}(r) = 0$, which results from the fact that the real electron-density $\hat{n}_e(r)$ ought to be an extremum of the thermodynamic potential $\Omega_e \equiv F_e - \mu_e N_e$, the muffin-tin potential $v_{\text{MT}}(r)$ is shown equal with the single-centre effective potential with use of some approximations

$$v_{\text{MT}}(r) \approx v_{\text{eN}}^{\text{eff}}(r)$$

$$= \widetilde{v}_{\text{eI}}(r) + \int \frac{C_{\text{ee}}(|r - r'|)}{-\beta} n_0^e [g_{\text{eI}}(r') - 1] \, dr'$$

$$+ \int \frac{C_{\text{eI}}(|r - r'|)}{-\beta} n_0^I [g_{\text{II}}(r') - 1] \, dr' . \tag{3.62}$$

Due to (3.62) the third term in the right-hand side of (3.58) disappears ultimately, and the kinetic energy difference is expressed in a simple form

$$\Delta T_s[\hat{n}_b^f] = \sum_{n \in \text{bound}} f(\widetilde{\epsilon}_n)\widetilde{\epsilon}_n - \sum_{\alpha=1}^{N} \sum_{n \in \text{bound}} f(\epsilon_n^{(\alpha)})\epsilon_n^{(\alpha)}$$

$$= \sum_{\alpha} \sum_{\ell \in \text{bound}} \int_{-\infty}^{\infty} (\epsilon - \epsilon_\ell^{(\alpha)}) n_{\ell\alpha}(\epsilon) f(\epsilon) d\epsilon \tag{3.63}$$

where $n_{\ell\alpha}(\epsilon)$ is a local-density of states on the orbital ℓ at α-site in the tight-binding approximation. On the other hand, the exchange–correlation energy in (3.50) is written in the cluster expansion

$$E_{\text{XC}}[\sum_{\alpha} \rho_b(r - R_\alpha)] = \sum_{\alpha} E_{\text{XC}}[\rho_b(r - R_\alpha)] + \frac{1}{2} \sum_{\alpha \neq \beta} (E_{\text{XC}}[\rho_b(r - R_\alpha) + \rho_b(r - R_\beta)]$$

$$- E_{\text{XC}}[\rho_b(r - R_\alpha)] - E_{\text{XC}}[\rho_b(r - R_\beta)])$$

$$+ \frac{1}{3!} \sum_{\alpha \neq \beta \neq \gamma} \left(\cdots\right) + \cdots \tag{3.64}.$$

Retaining the binary term only in (3.64), we end up with a formula to determine the core-overlap interaction in the TBB model [16, 17]

$$\Delta T_s[\hat{n}_b^f] + \Delta E_{\text{XC}}[\hat{n}_b^f]$$

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \left[\int \frac{Z_I(r) Z_I(r')}{|r - r' + R_{\alpha\beta}|} \, dr \, dr' - \frac{Z_I^2}{R_{\alpha\beta}} \right]$$

$$= \sum_{\alpha} \sum_{\ell \in \text{bound}} \int_{-\infty}^{\infty} (\epsilon - \epsilon_\ell^{(\alpha)}) n_{\ell\alpha}(\epsilon) f(\epsilon), \, d\epsilon$$

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} u_{\text{rep}}(|R_\alpha - R_\beta|) \tag{3.65}$$

where $u_{\rm rep}(r)$ is a short-range repulsive potential provided by the exchange–correlation and electrostatic contibutions as follows

$$u_{\rm rep}(R_{\alpha\beta}) \equiv E_{\rm XC}[\rho_{\rm b}(r-R_\alpha)+\rho_{\rm b}(r-R_\beta)] - E_{\rm XC}[\rho_{\rm b}(r-R_\alpha)] - E_{\rm XC}[\rho_{\rm b}(r-R_\beta)]$$

$$+ \int \frac{Z_{\rm I}(r)Z_{\rm I}(r')}{|r-r'+R_{\alpha\beta}|}\,{\rm d}r\,{\rm d}r' - \frac{Z_{\rm I}^2}{R_{\alpha\beta}}\,. \qquad (3.66)$$

3.3. The relation between the single- and multi-centre problems

When the DF theory is applied to the single-centre problem of a coupled nucleus–electron system with a fixed nucleus at the origin, the ion–ion and electron–ion RDFs are determined in conjunction with the bound electron distribution $\rho_{\rm b}(r)$, the muffin-tin potential $v_{\rm MT}(r) = v_{\rm eI}^{\rm eff}(r)$ of (3.62) and the DCF $C_{\rm eI}(r)$, which are necessary as input data to investigate the multi-centre problem. Next, with use of these quantities, the DF theory can deal with the multi-centre problem to determine the electronic structure in the presence of randomly distributed nuclei: also, the effective Hamiltonian for a quasi-one-component classical fluid, the core-overlap interaction, the thermodynamic quantities and the density of states can be evaluated at this process. Note that the single-centre and multi-centre problems are coupled with each other; the core-overlap interaction (3.50) produces a bare ion–ion interaction (3.53), which is used as an input to the single-centre problem as discussed in section 3.1. The electron density distribution $n_{\rm e}(r|R_1\cdots R_N)$ in the presence of randomly distributed nuclei at $\{R_\alpha\}$ is represented by the Green function for this system

$$n_{\rm e}(r|R_1\cdots R_N) = -\frac{1}{\pi}\,{\rm Im}\int_{-\infty}^{\infty} f(\epsilon)G(r,r;\epsilon)\,{\rm d}\epsilon\,. \qquad (3.67)$$

The configuration-averaged electron density $\langle n(r|R_1\cdots R_N)\rangle_{R_1=0}$, under the condition that a nucleus is fixed at the origin, should be equal with the total electron density around a fixed nucleus $n_{\rm e}^T(r|U_{\rm ext}=-Z_{\rm A}/r)$ calculated from the single-centre problem:

$$n_{\rm e}^T(r|{\rm N}) \equiv n_{\rm e}(r|U_{\rm ext}=-Z_{\rm A}/r) + n_0^1\int \rho_{\rm b}(r-r')g_{\rm II}(r')\,{\rm d}r'$$

$$= \langle n(r|R_1\cdots R_N)\rangle_{R_1=0} = -\frac{1}{\pi}\,{\rm Im}\int_{-\infty}^{\infty} f(\epsilon)\langle G(r,r;\epsilon)\rangle_{R_1=0}\,{\rm d}\epsilon\,.$$

$$(3.68)$$

It may be physically ascribed to (3.68) that the effective potential $v_{\rm eN}^{\rm eff}(r)$ of (3.9), derived in the single-centre problem, becomes at the same time a self-consistent potential for the multi-centre problem in the summing form of muffin-tin potentials for each nucleus, since the muffin-tin potential at the origin should be a functional of the density distribution $\langle n(r|R_1\cdots R_N)\rangle_{R_1=0}$. In addition, there is another relation between single- and multi-centre quantities: the bound electron number $Z_{\rm B}$ determined by the single-centre problem is equal with that evaluated by the use of the local density of states obtained in the multi-centre system

$$Z_{\rm B} = \int \rho_{\rm b}(|r-R_\alpha|)\,{\rm d}r = \sum_{i\in{\rm inner\ core}} f(\tilde{\epsilon}_i) + \sum_{l}\int_{-\infty}^{\infty} n_{l\alpha}(\epsilon)f(\epsilon)\,{\rm d}\epsilon \qquad (3.69)$$

which is assumed also in (3.63), where 'inner core' implies inner bound levels almost unaltered both for single- and multi-potentials. Therefore, the ionization can be considered to be defined by both single- and multi-centre problems; both definitions should give the same ionization when two problems are solved in a self-consistent manner.

The structure of a neutral liquid can be investigated by solving coupled single- and multi-centre problems; a formulation for a neutral fluid is obtained by taking limit of the conduction-electron number zero in the previous result. By taking this limit of the DCF $C_{eI}(r)$, we obtain the relation

$$
\begin{aligned}
-\lim_{n_0^e \to 0} C_{eI}(r) &= -\lim_{n_0^e \to 0}\{\widehat{B}^{-1}[n_e^{0c}(r|v_{eN}^{\text{eff}})/n_0^e - 1] - \Gamma_{eI}(r)\} \\
&= \lim_{n_0^e \to 0}\beta\tilde{v}_{eI}(r) \\
&= \beta\left[-\frac{Z_A}{r} + \int v_{ee}^c(|r-r'|)\rho_a(r')\,\mathrm{d}r' + \mu_{\text{XC}}(\rho_a(r))\right] \\
&\equiv \beta\tilde{v}_{ea}(r) \ .
\end{aligned}
\tag{3.70}
$$

Thus, the bound electron distribution of a neural atom in a liquid is obtained in the form

$$
n_e^b(r) = \rho_a(r) = n_e^{0b}(r|v_{ea}^{\text{eff}})
\tag{3.71}
$$

by solving the wave equation for the potential $v_{ea}^{\text{eff}}(r)$, which results from the limit

$$
\lim_{n_0^e \to 0} v_{eN}^{\text{eff}}(r) = v_{ea}^{\text{eff}}(r) \equiv \tilde{v}_{ea}(r) + \int \tilde{v}_{ea}(|r-r'|)n_0[g(r')-1]\,\mathrm{d}r' \ .
\tag{3.72}
$$

Hence, the atomic interaction is determined by using $\rho_a(r)$ so obtained to express the electron distribution n^f by the superposition, $n^f(r) = \sum_{\alpha=1}^N \rho_a(r-R_\alpha)$, which is inserted in the GK formula as follows

$$
\Delta E[\hat{n}_e|R_1\cdots R_N] = \Delta T_s[n^f] + \Delta E_{\text{XC}}[n^f] + \frac{1}{2}\sum_{\alpha\neq\beta}\int \frac{Z_A(r)Z_A(r')}{|r-r'+R_{\alpha\beta}|}\,\mathrm{d}r\,\mathrm{d}r'
$$

$$
\approx \frac{1}{2}\sum_{\alpha\neq\beta} v_{\text{aa}}(|R_\alpha - R_\beta|) \ .
\tag{3.73}
$$

Once the interatomic potential is determined by (3.73), the RDF is finally represented by

$$
g(r) = \exp[-\beta v_{aa}(r) + \gamma(r) + B(r)]
\tag{3.74}
$$

in terms of the bridge function $B(r)$ and $\gamma(r) \equiv n_0 \int C(|r-r'|)[g(r')-1]\mathrm{d}r'$, which is related to the OZ relation, $g(r)-1 = C(r)+\gamma(r)$, with the DCF $C(r)$. It should be noted that the atomic electron density $\rho_a(r)$ is not the bound electron density of a free-atom, but of the atom immersed in a liquid as described by (3.71): equations (3.71), (3.73) and (3.74) must be solved self-consistently as a coupled problem of single- and multi-centre systems. This approach makes contrast with the method of Senatore *et al* [19], who determined $\rho_a(r)$ in treating the multi-centre problem. However, it should be remembered here that the GK method does not give the van der Waals tail of potential: to produce it, an additional procedure [20] is necessary to combine with the GK method.

3.4. The definition of ionization and resonant states

When a liquid metal or a plasma is taken as a binary 'ion'-electron mixture, the ionic charge Z_I should be defined so as to satisfy a general relation

$$Z_I S_{II}(0) = \sqrt{Z_I} S_{eI}(0) \tag{3.75}$$

which results from (2.11). By the inverse Fourier transform, this equation is rewritten in the form

$$Z_I = n_0^e \int (g_{eI}(r) - 1)\, dr - Z_I n_0^I \int (g_{II}(r) - 1)\, dr = Z_A - Z_B \tag{3.76}$$

which states that an ion fixed at the origin keeps the charge neutrality by accumulating the conduction electrons and by pushing away the ions around it in the whole space, not within the Wigner–Seitz cell. From the view point of the DF theory, the fixed central ion in a liquid metal produces an external potential of single-centre, while a fixed ion in a solid induces a multi-centre external potential; that is, all other ions are considered to be fixed together and to contribute to the formation of the external potential. Therefore, in a solid the space is to be divided into the Wigner–Seitz cells corresponding to each ion; in contrast with this situation, in a liquid the fixed ion has the whole space as its world in the determination of electronic structure and ionic configuration, without being confined in the Wigner–Seitz cell. Therefore, we can define the bound electron number within a single-centre problem in the whole space so as to fulfill the condition of the charge neutrality. In a simple metal, the bound electron number Z_B is evaluated from the bound electron distribution $\rho_b(r) = n_e^b(r|N)$ by $Z_B = \int_0^\infty \rho_b(r)\, dr$, that is,

$$Z_B \equiv \sum_{\epsilon_i < 0} \frac{1}{\exp[\beta(\epsilon_i - \mu_e^0)] + 1} \tag{3.77}$$

and the ionization is obtained by $Z_I \equiv Z_A - Z_B$ with a chemical potential μ_e^0 determined by

$$\lim_{r \to \infty} n_e^c(r|I) = \int \frac{2}{\exp[\beta(p^2/2m - \mu_e^0)] + 1} \frac{dp}{(2\pi\hbar)^3} = n_0^e = Z_I n_0^I . \tag{3.78}$$

It should be noted that in this definition the bound-state is simply defined by a state with $\epsilon_i < 0$; as a result, this definition of Z_I can be applied only to a 'simple metallic' system. The simple definition of Z_B by (3.77) has many problems to be improved: the bound electron number exhibits a discrete change when a bound state in a plasma begins to disappear with the increase of density by compression. Furthermore, equation (3.75) is rewritten for a liquid metal in another form related to the Friedel sum rule concerning phase shifts $\delta_\ell(E)$ at the Fermi energy E_F

$$Z_I S_{II}(0) = \int (n_e^c(r) - n_0^e)\, dr = Z_I n_0^I \kappa_T / \beta = \frac{2}{\pi} \sum_\ell (2\ell + 1)\delta_\ell(E_F) \tag{3.79}$$

where κ_T is a compressibility. In general, there is a resonant state [21, 22] which shows a strongly localized behaviour around a nucleus, although it belongs to continuum states. When a significant resonant state, with a large phase shift $\delta_\ell(E_F)$ at the

Fermi energy, appears in a liquid metal, the relation (3.79) can not be satisfied if we use a simple definition (3.77), since the compressibility is so small that $Z_I S_{II}(0) \approx 0$ in a liquid metal while the Friedel sum becomes large due to a resonant state. This fact indicates that some part of the Friedel sum due to a resonant state should be taken to be included as the 'bound' electron number in addition to Z_B defined by (3.77), since the following exact relation must be satisfied:

$$\int (n_e^b(r) + n_e^c(r) - n_0^e) dr = \sum_{\epsilon_i < 0} f(\epsilon_i) + \frac{2}{\pi} \sum_{\ell} (2\ell+1) \delta_\ell(E_F)$$

$$= Z_B + Z_I n_0^I \kappa_T / \beta . \tag{3.80}$$

In other words, this shows that some part of the conduction-electron distribution, which is to be assigned to physical resonant states, should be taken as the 'bound'-electron distribution $n_e^b(r|N)$ forming an 'ion' in such a way as to fulfill this relation. Thus, we are forced to take account of the localized contribution involved in a resonant state in the definition of an 'ion', when it becomes significant.

A precise definition of a resonant state [23] can be given by the S-matrix $S_\ell(E)$ concerning the wave equation for an electron under the effective potential (3.9) with $S_\ell(E) = \exp(2i\delta_\ell(E))$. The S-matrix has a branch line along the positive axis, and is analytic on a two sheeted Riemann surface except for poles which lie at $E = -|\epsilon_{n\ell}|$ representing bound states and for a infinite number of poles which are on the sheet reached via the cut along the positive real axis; the latter are attributed to the resonant states $\widetilde{E}_{n\ell} = \tilde{\epsilon}_{n\ell} - i \gamma_{n\ell}$. If a resonant pole has a small $\gamma_{n\ell}$ compared with $\tilde{\epsilon}_{n\ell}$, the resonant state shows almost the same behaviour to a bound state; hereafter this state is referred as a physical resonant state for convenience. More [21] has shown that the equilibrium thermal occupation probability $n(\widetilde{E}_{n\ell})$ of a resonant state $\widetilde{E}_{n\ell}$ can be given by the expression:

$$n(\widetilde{E}_{n\ell}) = 2(2\ell + 1) \operatorname{Re} F(\widetilde{E}_{n\ell}) \tag{3.81}$$

with

$$F(\widetilde{E}_{n\ell}) \equiv \frac{1}{i\pi} \int_0^\infty \left(\frac{E}{\widetilde{E}_{n\ell}} \right)^{1/2} \frac{f(E)}{E - \widetilde{E}_{n\ell}} dE \tag{3.82}$$

where $\sqrt{\widetilde{E}_{n\ell}}$ means the principal root. The expression $\operatorname{Re}[F(\widetilde{E}_{n\ell})]$ is an extension of the Fermi distribution $f(\epsilon)$ for a real energy ϵ to a complex-energy state, since $\lim_{\gamma \to 0^+} \operatorname{Re}[F(\epsilon + i\gamma)] = f(\epsilon)$. Thus we can rewrite (3.80) in terms of the generalized Fermi distribution $F(\widetilde{E}_{n\ell})$

$$\int (n_e^b(r) + n_e^c(r) - n_0^e) dr = \sum_{\epsilon_i < 0} f(\epsilon_i) + \sum_{\ell} 2(2\ell + 1) \sum_{n \in \text{res}} \operatorname{Re}[F(\widetilde{E}_{n\ell})]$$

$$= Z_B + Z_I n_0^I \kappa_T / \beta \tag{3.83}$$

because of the relation [21]

$$\sum_{n \in \text{res}} \operatorname{Re}[F(\widetilde{E}_{n\ell})] = \frac{1}{\pi} \int_0^\infty f(E) \frac{d\delta_\ell(E)}{dE} dE \tag{3.84}$$

$$= \frac{\delta_\ell(E_F)}{\pi} \qquad (\text{for } T = 0) . \tag{3.85}$$

As a result, it is required by (3.83) that the 'bound'-electron number Z_B in an ion should involve a contribution of the physical resonant states ($|\operatorname{Im} \widetilde{E}_{n\ell}| \ll \operatorname{Re} \widetilde{E}_{n\ell}$) in addition to the core electrons with $\epsilon_i < 0$ in such a way that

$$Z_B \equiv \sum_{\epsilon_i < 0} f(\epsilon_i) + \sum_{n\ell \in \text{phys.res.}} 2(2\ell+1) \operatorname{Re}[F(\widetilde{E}_{n\ell})] . \tag{3.86}$$

Here, the chemical potential μ_e^0 is determined by

$$Z_A = \sum_{\epsilon_i < 0} \frac{1}{\exp[\beta(\epsilon_i - \mu_e^0)] + 1} + \sum_{n\ell \in \text{phys.res.}} 2(2\ell+1) \operatorname{Re}[F(\widetilde{E}_{n\ell})]$$

$$+ \frac{1}{n_0^I} \int \frac{2}{\exp[\beta(p^2/2m - \mu_e^0)] + 1} \frac{dp}{(2\pi\hbar)^3} \tag{3.87}$$

if $|\varphi_{n\ell}^2(R_c)| \approx 0$, where R_c is a correlation length defined later. To be consistent with (3.86), the left-side hand of (3.83) requires that the 'bound'-electron distribution $n_e^b(r|N)$ should be taken as composed of the states with $\epsilon_i < 0$ and the physical resonant states with complex energies $\widetilde{E}_{n\ell}$, as is written in the form [21]

$$n_e^b(r|N) = \sum_{\epsilon_i < 0} f(\epsilon_i)|\phi_i(r)|^2 + \sum_{n\ell \in \text{phys.res.}} \frac{2(2\ell+1)}{4\pi r^2} \operatorname{Re}[F(\widetilde{E}_{n\ell})\varphi_{n\ell}^2(r)] \tag{3.88}$$

where $\varphi_{n\ell}(r)$ denotes a resonant wavefunction which obeys the wave equation with a complex eigenvalue $\widetilde{E}_{n\ell}$. However, it should be kept in mind that a resonant wavefunction can not be normalized in the whole space in a usual way because of the behaviour in the large distances: $\lim_{r\to\infty} |\varphi_{n\ell}(r)| \to \infty$. Since the electron–ion correlation can be considered to become uncorrelated outside the correlation length R_c, the integral in (3.83) are taken to be performed up to this distance R_c to treat the resonant states. Then, the bound electron number (3.86) becomes equal with $Z_B = \int_0^{R_c} \rho_b(r)\,dr$, since the resonant functions $\varphi_{n\ell}(r)$ are known to be almost real, normalized and orthogonal functions on a fixed interval $0 < r < R_c$, if the resonance lifetimes are sufficiently long [21]. At this point an important remark is made that the bound electron number given by (3.86) varies continuously when a bound state with $\epsilon_i < 0$ disappears into the continuum state by the compression of a plasma, since the disappearing pole associated with a bound state turns out to become a resonant pole at that time.

In this connection, Moriarty [24] proposed the number of bound electrons retained by the ion in a transition metal with 3d-resonant electrons, for example, to be $Z_B = \sum_{\epsilon_i < 0} f(\epsilon_i) + 10\delta_d(E_F)/\pi$; this definition follows from (3.86) by the approximation

$$\operatorname{Re}[F(\widetilde{E}_{3d})] \approx \sum_{n' \in \text{res.}} \operatorname{Re}[F(\widetilde{E}_{n'd})] = \frac{\delta_d(E_F)}{\pi} \qquad \text{(for } T = 0\text{)} \tag{3.89}$$

which is justified when widths of other resonant states than the 3d-state are all large. Moreover, Moriarty approximated the d-resonant wavefunctions by the localized wavefunctions (the zeroth-order pseudoatom) obtained by adding the localization potential to the single-centre potential (3.9) so as to produce a bound-state like wavefunction. In some similar way to Moriarty, resonant wavefunctions are necessary to

be approximated by bound-state-like wavefunctions in order to be actually used in the TBB model. However, it may be possible that the tight-binding formulation is generalized in terms of resonant wavefunctions in spite of their unphysical tail behaviour, since the matrix elements of an arbitrary operator between resonant states can be defined with use of special technique ([22] p 153 ff).

4. Summary and discussion

We have formulated a method to treat a non-simple liquid metal and plasma in a unified manner including also a neutral liquid as a special case; the RDF, the ionic charge and the muffin-tin potential are determined by solving a single-centre problem with a bare ion–ion interaction as an input, while the density of states, the bare ion–ion interaction and thermodynamic properties are to be obtained as results of the multi-centre problem with use of output from the single-centre problem. The RDF, $g_{II}(r)$ and $g_{eI}(r)$, are given by (2.18) with a bare ion–ion interaction (3.53) and (2.19) with an electron–ion interaction (2.22), respectively. Clearly speaking, the $g_{eI}(r)$ is the conduction-electron density distribution $n_e^c(r|N)$ under the effective potential (3.99), and the bound electron distribution $n_e^b(r|N)$ given by (3.88) provides the electronic structure $\rho_b(r)$ of an ion with the ionic charge determined by (3.86): a 'bound' state is defined as a state of a discrete energy level with $\epsilon_i < 0$ or as a physical resonant state of a complex energy with $|\operatorname{Im} \tilde{E}_{n\ell}| \ll \operatorname{Re} \tilde{E}_{n\ell}$. Once the this single-centre problem is solved, the muffin-tin potential for the multi-centre problem is obtained by (3.62) in terms of the DCFs and single-centre quantities; thus, the generalized TBB model (3.65) or the GK model (3.50) can determine the core-overlap interaction, which yields the bare ion–ion interaction (3.53) to be used in the single-centre problem. In this way, the single- and multi-centre problems are coupled with each other, and produce a set of integral equations for ion-configurational and electronic structures in conjunction with the internal structure of an ion for liquid metals or plasmas, in principle. The internal energy of a liquid metal is shown to be expressed in terms of single-centre quantities as (3.54) in the multi-centre treatment. In our approach, however, it becomes natural to treat the single-centre problem independently from the multi-centre problem for a 'simple metallic' system, where the ion–ion potential is taken to be purely Coulombic, since the core-electron overlap is negligible and no significant resonant state appears there. In our formulation, the bound electron number Z_B is defined by (3.86) in the single-centre problem. However, it can be defined also in the multi-centre system in terms of a local density of states $n_{i\alpha}(\epsilon)$, and two definitions should yield the same result as discussed in section 3.3

$$Z_B \equiv \sum_{\epsilon_i < 0} f(\epsilon_i) + \sum_{n\ell \in \text{phys.res.}} 2(2\ell + 1) \operatorname{Re}[F(\tilde{E}_{n\ell})] \qquad (4.1)$$

$$= \sum_{i \in \text{inner core}} f(\tilde{\epsilon}_i) + \sum_\ell \int_{-\infty}^\infty \langle n_{\ell\alpha}(\epsilon) \rangle f(\epsilon) \, d\epsilon \qquad (4.2)$$

when the single- and multi-centre problems are solved self-consistently.

We have shown that the effective electron-nucleus interaction (3.9) determined by the single-centre treatment can be used as a self-consistent muffin-tin potential

(3.62) for the multi-centre problem. This fact indicates that we need not solve the multi-centre problem iteratively to get a self-consistent potential, since it can be obtained by solving the single-centre problem. With this respect, we remark that the effective electron-nucleus interaction (3.62) is shown to be rewritten approximately in the form like (3.72) representing an effective potential for electrons caused by the superposition of neutral pseudoatoms including the bound electrons [7] as is done by the Mattheiss procedure to construct the muffin-tin potential from a free-atom potential in the energy band calculation of a solid. Also, it is important to note that self-consistent base functions in the TBB method and a self-consistent bound electron density $n_b(r)$ in the GK method may be obtained by the use of the effective potential (3.62); the kinetic energy difference of the system ΔT_s from that of isolated ions can be represented only by the variation of energy levels as described by (3.63) in the TBB model, if we use the self-consistent base functions determined by this single-centre potential (3.62). When we treat a transition metal, for example, the core-overlap interaction is described in terms of physical resonant states in our formulation. However, they cannot be used as usual base functions in the tight-binding approximation, since a resonant wavefunction has a unphysical tail behaviour. Therefore, a resonant wavefunction is necessary to be approximated by a bound-state-like wavefunction, as was done by several investigators [24, 25], in order to be used for the tight-binding model in a usual way. On the contrary, the TBB method may be extended to be performed by using resonant wavefunctions as the base functions with the help of some procedure such as the complex coordinate method [26].

With use of the nucleus–electron model the internal energy of a liquid metal is derived as (3.54), which is different from the usual internal energy formula based on the pseudopotential theory in that the term $N n_0^e w_b^R(Q=0)$ representing the core-electron–conduction-electron interaction in terms of the pseudopotential $w_b(r) \equiv w_b^R(R) - Z_I/r$ is replaced by $N n_0^e \tilde{v}_{el}^R(Q=0)$ in (3.54), the Fourier transform of the non-Coulomb part of the bare electron–ion interaction (2.22). It should be mentioned that the interaction between conduction- and core-electrons in the core region cannot be precisely represented by the pseudopotential $w_b(r)$ in contrast with $\tilde{v}_{el}(r)$ of (2.22) being valid there, since the pseudopotential is appropriate to express electron–ion interaction only outside of the core region. Therefore, the core-electron–conduction-electron interaction term in the internal energy is not adequately given by the pseudopotential $w_b(r)$. Because of this difference, the internal energy (3.54) of a liquid metal in the nucleus–electron model is rewritten using the compressibility κ_T^e of an electron gas with a different volume energy U_v from that of the pseudopotential theory

$$U_v/N = (T_s[n_0^e] + E_{XC}[n_0^e])/N - \frac{1}{2}\frac{Z_I}{n_0^e \kappa_T^e} + \frac{1}{2}v_{ind}(r=0)$$

$$+ n_0^e \left[\tilde{v}_{el}^R(Q=0) - \frac{C_{el}^R(Q=0)}{-\beta} \right] \qquad (4.3)$$

in the form

$$E = \tfrac{1}{2} N n_0^I \int v^{eff}(r) g_{II}(r)\, dr + \tfrac{3}{2} k_B T N + N \epsilon_{ion} + U_v \,. \qquad (4.4)$$

Here, the last term of (4.3) with $C_{el}^R(Q) \equiv C_{el}(Q) - \beta 4\pi Z_I/Q^2 \approx -\beta w_b^R(Q)$ remains as uncanceled in contrast with the pseudopotential theory. Recently, Walker

and Taylor [27] have shown that the internal energy of a simple metal can not be adequately represented by the expression based on the first-principles non-local pseudopotential, and the volume energy should be corrected to take account of the core-electron–conduction-electron interaction; the relation of this correction to the last term of (4.3) is to be investigated in a future work. On the other hand, the internal energy for 'non-simple metallic' system is written with the help of (3.65) in the form appropriate to express the bonding energy

$$E = \tfrac{1}{2} N n_0^{\mathrm{I}} \int [v_{\mathrm{II}}^{\mathrm{c}}(r) + v_{\mathrm{ind}}(r)] g_{\mathrm{II}}(r) \mathrm{d}r + \tfrac{3}{2} k_{\mathrm{B}} T N + N \epsilon_{\mathrm{ion}}$$

$$+ U_{\mathrm{v}} + U^{\mathrm{bond}} + U^{\mathrm{rep}} \tag{4.5}$$

where

$$U^{\mathrm{bond}} = \langle \Delta T_{\mathrm{s}}[\hat{n}_{\mathrm{b}}^{f}] \rangle = \sum_{\alpha} \sum_{\ell \in \mathrm{bound}} \int_{-\infty}^{\infty} (\epsilon - \epsilon_{\ell}^{(\alpha)}) \langle n_{\ell\alpha}(\epsilon) \rangle f(\epsilon) \, \mathrm{d}\epsilon \tag{4.6}$$

$$U^{\mathrm{rep}} = \tfrac{1}{2} N n_0^{\mathrm{I}} \int u_{\mathrm{rep}}(r) g_{\mathrm{II}}(r) \, \mathrm{d}r \; . \tag{4.7}$$

When the ion–ion RDF $g_{\mathrm{II}}(r)$ is approximated by the step function $\theta(r - R_{\mathrm{WS}})$ with the Wigner–Seitz radius R_{WS}, $g_{\mathrm{II}}(r) \approx \theta(r - R_{\mathrm{WS}})$, in the effective electron–nucleus interaction (3.9) in addition to the approximation $C_{\mathrm{eI}}(r) \approx -\beta v_{\mathrm{eI}}^{\mathrm{c}}(r)$, the effective potential (3.9) reduces to a potential caused by a fixed nucleus at the centre of a spherical vacancy in the jellium model

$$v_{\mathrm{eN}}^{\mathrm{eff}}(f) \approx -\frac{Z_{\mathrm{A}}}{r} + \int v_{\mathrm{ee}}^{\mathrm{c}}(|r - r'|)[n_{\mathrm{e}}(r') - n_0^{\mathrm{e}} \theta(r' - R_{\mathrm{WS}})] \, \mathrm{d}r'$$

$$+ \mu_{\mathrm{XC}}(n_{\mathrm{e}}(r)) - \mu_{\mathrm{XC}}(n_0^{\mathrm{e}}) \; . \tag{4.8}$$

This jellium-vacancy model is shown to yield a good non-linear pseudopotential $-C_{\mathrm{eI}}(r)/\beta$ to give an effective ion–ion interaction (2.20) in a simple metal [5]. For a non-simple liquid, also, the jellium-vacany model may afford to give the non-linear pseudopotential and the bound electron distribution (3.88) involving resonant states without coupling to the multi-centre problem; these results are to be used as initial input data for the coupled problem of single- and multi-centre systems.

When a bare ion–ion interaction determined by (3.50) becomes a three-body force, our formulation may be incorporated in integral equations for a fluid with a three-body interaction as was given by many investigators [28]. In treating a liquid metal, it is a standard approximation to replace the LFC $G(Q)$ by that of the jellium model where the presence of ions are taken to be a uniform positive background: the two component nature is neglected in this replacement. When the electron temperature is increased for electrons to behave as a classical fluids, or when the electron–ion interaction is significant as is a case of a liquid metallic hydrogen, this approximation will break down, and an integral equation to determine the DCF $C_{\mathrm{ee}}(r)$ is necessary to be set up as was done in the previous works [2, 3].

Appendix. Proof of (2.1)

The Hamiltonian of a binary mixture composed of N ions and N_e electrons is written as

$$\hat{H} = \hat{K}_I + \hat{V}_{II}(\hat{R}^N) + \hat{H}_e + \hat{V}_{eI}(\hat{r}^{N_e}, \hat{R}^N) \tag{A1}$$

where

$$\hat{V}_{II}(\hat{R}^N) \equiv \frac{1}{2} \sum_{\alpha \neq \beta} v_{II}(|\hat{R}_\alpha - \hat{R}_\beta|) \tag{A2}$$

$$\hat{H}_{ee} \equiv \sum_{i=1}^{Z_I N} \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\hat{r}_i - \hat{r}_j|} \tag{A3}$$

$$\hat{V}_{eI}(\hat{r}^{N_e}, \hat{R}^N) \equiv \sum_{\alpha=1}^{N} \sum_{i=1}^{N_e} v_{eI}(|\hat{r}_i - \hat{R}_\alpha|) \tag{A4}$$

and K_I denotes the kinetic energy of the ions: the ions are taken to be classical particles. The ions can be treated as classical particles, when the thermal wavelength $\lambda = (\beta h^2 / 2\pi M)^{1/2}$ of ion in a liquid is sufficiently small compared with the average interatomic distance a and the characteristic length ℓ of interacting potential of the system. Because of $[\hat{P}_\alpha, \hat{R}_\alpha] = 0$, the canonical partition function of the ion–electron mixture is expressed in the $\{rR\}$-representation with $|rR\rangle \equiv |r_1 \cdots r_{N_e} R_1 \cdots R_N\rangle$ as follows

$$Q_N = \text{Tr} \exp(-\beta \hat{H})$$

$$= \int dr^{N_e} dR^N \langle rR| \exp(-\beta \hat{H})|rR\rangle \tag{A5}$$

$$= \int dR^N \langle R| \exp[-\beta(\hat{K}_I + \hat{V}_{II})]|R\rangle$$

$$\times \left\langle r \left| \exp\left[-\beta\left(\hat{H}_e + \sum_{i,\alpha} v_{eI}(|\hat{r}_i - R_\alpha|)\right)\right] \right| r \right\rangle \tag{A6}$$

$$= \frac{\lambda^{-3N}}{N!} \int dR^N \exp\left[-\beta\left(\frac{1}{2} \sum_{\alpha \neq \beta} v_{II}(|R_\alpha - R_\beta|)\right)\right]$$

$$\times \text{Tr}_e^{Z_I N} \exp\left[-\beta\left(\hat{H}_e + \sum_{i,\alpha} v_{eI}(|\hat{r}_i - R_\alpha|)\right)\right] \tag{A7}$$

where $\text{Tr}_e^{Z_I N}$ refers to a complete set of electronic states with $N_e = Z_I N$. Here, we used the relation for classical particles, that is, for a fluid with $\lambda \ll a$ and $\lambda \ll \ell$ (see [29], for example)

$$\int dR^N \langle R| \exp[-\beta(\hat{K}_I + \beta \hat{V}_{II})]|R\rangle = \frac{1}{N! h^{3N}} \int dP^N dR^N$$

$$\times \exp\left[-\beta\left(\sum_{\alpha=1}^{N} \frac{P_\alpha^2}{2M} + \frac{1}{2} \sum_{\alpha \neq \beta} v_{II}(|R_\alpha - R_\beta|)\right)\right]. \tag{A8}$$

Thus, the grand partition function for this homogeneous mixture is given by

$$
\Xi[0] \equiv \sum_{N=0}^{\infty} \frac{z^N}{N!} \int dR^N \exp(-\beta \hat{V}_{\mathrm{II}}(R^N))
$$

$$
\times \operatorname{Tr}_e^{Z_{\mathrm{I}}N} \exp\left[-\beta\left(\hat{H}_e + \sum_{i,\alpha} v_{\mathrm{eI}}(|\hat{r}_i - R_\alpha|) - \mu_e Z_{\mathrm{I}}N\right)\right] \tag{A9}
$$

with a fugacity $z = \exp(-\beta\mu_{\mathrm{I}})/\lambda^3$, under the condition of the charge neutrality, $\langle \hat{N}_e \rangle = Z_{\mathrm{I}}\langle \hat{N} \rangle$, being fulfilled. Here, let us treat an inhomogeneous fluid created by adding an ion at $x = R_{N+1}$ to the ion–electron mixture with additional Z_{I} electrons to keep the system neutral; then, the grand partition function of this inhomogeneous mixture is associated with that of the homogeneous system $\Xi[0]$ as shown below

$$
\Xi[U_\alpha = v_{\alpha I}] = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int dR^N \exp\left[-\beta\left(\hat{V}_{\mathrm{II}}(R^N) + \sum_{i=1}^{N} v_{\mathrm{II}}(|R_i - R_{N+1}|)\right)\right]
$$

$$
\times \operatorname{Tr}_e^{Z_{\mathrm{I}}(N+1)} \exp\left[-\beta\left(\hat{H}_e + \sum_{i,\alpha} v_{\mathrm{eI}}(|\hat{r}_i - R_\alpha|)\right.\right.
$$

$$
\left.\left. + \sum_{j=1}^{Z_{\mathrm{I}}(N+1)} v_{\mathrm{eI}}(|\hat{r}_j - R_{N+1}|) - \mu_e Z_{\mathrm{I}}(N+1)\right)\right]
$$

$$
= n_0^{\mathrm{I}} \Xi[0]/z . \tag{A10}
$$

Due to the above equation, we can prove that the electron–ion RDF $g_{\mathrm{eI}}(|r - x|)$ becomes identical with the inhomogeneous electron-density distribution $n_e(r|\mathrm{I})/n_0^e$ caused by the ion fixed at $x = R_{N+1}$ as follows

$$
n_e(r|\{U_\alpha = v_{\alpha I}\}) = \left\langle \sum_i \delta(r - \hat{r}_i) \right\rangle_{U_\alpha = v_{\alpha I}}
$$

$$
= \frac{1}{\Xi[U_\alpha]} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int dR^N \exp[-\beta \hat{V}_{\mathrm{II}}(R^{(N+1)})]
$$

$$
\times \operatorname{Tr}_e^{Z_{\mathrm{I}}(N+1)} \left[\sum_i \delta(r - \hat{r}_i)\right]
$$

$$
\times \exp\left[-\beta\left(\hat{H}_e + \sum_{i,\alpha} v_{\mathrm{eI}}(|\hat{r}_i - R_\alpha|) - \mu_e Z_{\mathrm{I}}(N+1)\right)\right]
$$

$$
= \frac{1}{z\, \Xi[U_\alpha = v_{\alpha I}]} \left\langle \sum_{i,\alpha} \delta(r - \hat{r}_i)\delta(x - \hat{R}_\alpha) \right\rangle \Xi[0] \tag{A11}
$$

$$
= n_0^e g_{\mathrm{eI}}(|r - x|) . \tag{A12}
$$

In a similar manner, we can prove the relation $g_{\mathrm{II}}(r) = n_{\mathrm{I}}(r|\mathrm{I})/n_0^{\mathrm{I}}$ for the ion–electron mixture with a fixed ion at the origin.

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