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Average atom model based on Quantum Hyper-Netted Chain method

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ABSTRACT

The study shows how to define, without any *ad hoc* assumption, the average ion charge Z_{I} in the electron-ion model for plasmas and liquid metals: this definition comes out of the condition that a plasma consisting of electrons and nuclei can be described as an electron–ion mixture. Based on this definition of the average ion charge, the Quantum Hyper-Netted Chain (QHNC) method takes account of the thermal ionization and the resonant-state contribution to the bound electrons forming an ion.

On the other hand, Blenski and Cichocki (2007) have derived a formula to determine the uniform electron density in a plasma as an electron–ion mixture by using the variational method with the help of the local density approximation. Without use of any approximation, we derived the formula determining the electron density in an extended form on the basis of the density functional theory. This formula is shown to be valid also for the QHNC method.

1. Introduction

A liquid metal or a plasma can be taken as a mixture of electrons and ions with uniform ion density n_0^{I} and electron density n_0^{e}. This binary mixture consists of ions with a definite ionic charge Z_{I} and the free electrons, interacting with each other via *binary* potentials $v_{ij}(r)$ $[i,j=\mathrm{I}$ or $\mathrm{e}]$ under the charge neutrality condition $n_0^{\mathrm{e}}=Z_{\mathrm{I}}n_0^{\mathrm{I}}$. Also, the ions are assumed to behave as *classical* particles, while the free electrons form a quantum fluid changed into a classical fluid at high temperature. We call this mixture "the electron-ion model" for a plasma. Although it is important to calculate the average ion-charge Z_{I} in a plasma for description of thermodynamic quantities, there is no established method to determine Z_{I} in the electron–ion model at the present time. In this work, we show how to obtain the definition of the average ion-charge Z_{I} in the electron–ion model. Under some conditions only, a plasma as an electron-nuclei mixture can be treated as an electron-ion mixture on the basis of the electron–ion model. This condition itself provides the definition of an "average ion" in the electron–ion model. To establish this definition, we need the radial distribution functions (RDF) as already known quantities in an electron–ion mixture with the given electron–ion and ion–ion interactions, $v_{\mathrm{eI}}(r)$ and $v_{\mathrm{II}}(r)$. In this regard, the quantum hyper-netted (QHNC) method [1] can determine the RDFs in the mixture for arbitrary interactions $v_{ij}(r)$ [even for charged hard-core potentials]. On the other hand, Saumon and coworkers [2] have calculated Z_{I} with the use of the QHNC method on the basis of some *ad hoc* assumptions about a separation of the bound electron density distribution from the total electron density distribution around a nucleus in a plasma: these assumptions can be avoided by use of the present definition of Z_{I}.

The QHNC method can produce the plasma structure including Z_{I} at arbitrary temperature T and ionic density n_0^{I} from the atomic number Z_{A} as an only input [3]. It should be emphasized that the QHNC method yields structure factors in good agreement with experiments for simple metals [4–6]. Also, this method can determine the electron–electron correlation in a consistent way with the ionic structure without the use of jellium model for electrons [7–9]. However, the QHNC method has the following two weak points, to be improved, about the determination of Z_{I} and a bootstrap relation to generate the electron–electron correlation consistent with the ion structure, as follows:

(I) In the QHNC method, the ionic charge $Z_{\mathrm{I}}=Z_{\mathrm{A}}-Z_{\mathrm{B}}$ is simply defined from $Z_{\mathrm{B}}\equiv\int n_{\mathrm{e}}^{\mathrm{b}}(r)d\mathbf{r}$ using the bound-electron density $n_{\mathrm{e}}^{\mathrm{b}}(r)$ for the wave equation. Therefore, this definition does not take account of the contribution of resonant states to Z_{B}. On the other hand, Blenski and coworkers [10–12] have derived an equation to determine the electron density n_0^{e} in a plasma by using the variational method (VAAQP model). Although the VAAQP model provides $Z_{\mathrm{I}}=n_0^{\mathrm{e}}/n_0^{\mathrm{I}}$ and Z_{B}, it cannot give the bound-electron distribution $\rho_{\mathrm{b}}(r)$ to fulfill $Z_{\mathrm{B}}=\int\rho_{\mathrm{b}}(r)d\mathbf{r}$ and, thus, the ion–ion correlation $g_{\mathrm{II}}(r)$. In this work, we derived two relations which are valid within the framework of the density functional (DF) theory and the electron–ion model.

(a): In the electron–ion model, the average ion charge Z_{I} is defined as

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$$Z_I = \frac{n_0^e}{n_0^I} = Z_A - \int [n_e(r) - n_0^e g_{eI}(r)] d\mathbf{r} = Z_A - \int \rho_b(r) d\mathbf{r} \tag{1}$$

$$\rho_b(r) \equiv n_e(r) - n_0^e g_{eI}(r). \tag{2}$$

This relation is derived from the necessary condition that a plasma consisting of electrons and nuclei can be described as a mixture of electrons and ions. At the same time, Eq. (1) is rewritten in the equivalent relation:

$$Z_A = \int [n_e(r) - n_0^e g_{II}(r)] d\mathbf{r}. \tag{3}$$

Here, $g_{eI}(r)$ and $g_{II}(r)$ are the electron–ion and ion–ion RDFs, respectively, in the electron–ion model, and $n_e(r)$ is the electron density distribution around the nucleus, when a chosen ion in this mixture is thought as an inserted atom with a nucleus Z_A.

(b): The uniform density n_0^e in the electron–ion model must satisfy the following condition:

$$\int v_{es}(r) g_{II}(r) d\mathbf{r} = \mu S_{II}(0)/n_0^I = \mu \kappa_T/\beta, \tag{4}$$

with $S_{II}(Q)$ being the structure factor. The above equation is reduced to the result of Blenski et al., when we make approximations, $g_{II}(r)$ by the step-function and $S_{II}(0) = 0$. Equations (1) and (4) solve the problem to determine the average ion charge Z_I.

(II): The QHNC method uses the following bootstrap relation to determine the electron–electron response function $\chi_{ee}(Q)$ from the electron density distribution $n_e(r|e)$ around a fixed electron in a plasma:

$$\mathcal{F}_Q[n_e(r|e) - n_0^e] \equiv \int [n_e(r|e) - n_0^e] \exp(i\mathbf{Qr}) d\mathbf{r} = \chi_{ee}(Q)/\chi_Q^0 - 1 \tag{5}$$

with the density response function χ_Q^0 of a non-interacting system. This relation results from the approximation used by Kukkonen and Overhauser [13,14] for an electron gas. Since Eq. (5) is an exact relation for a classical electron gas, it is appropriate in treating a high-temperature plasma. Therefore, the QHNC method with the use of Eq. (5) provides a good description of the pair correlations for a hydrogen-plasma gas at low densities and high temperatures where the electrons behave as a classical electron gas [15]. However, Eq. (5) contains an approximation that the fixed electron in a liquid metal has the exchange effect to surrounding electrons: the exchange-effect part must be subtracted in the form:

$$\mathcal{F}_Q[n_e(r|\hat{e}) - n_0^e] = \chi_{ee}(Q)/\chi_Q^0 - 1 - n_0^e \beta v_{ee}(Q) G_x(Q) \chi_Q. \tag{6}$$

Here, $G_x(Q)$ is the exchange part of the local field correction. If we approximate $G_x(Q)$ by the use of $G_x^{jell}(Q)$, which is well known for an electron gas in the jellium model, the QHNC method yields a closed set of equations for plasma properties. To get a closed set of equations to determine all quantities in a self-consistent manner, it is necessary to build up a new equation for $G_x(Q)$.

2. Charge neutrality condition in the electron–ion model

At first, we note exact relations between the structure factors $S_{ij}(Q)$ in the electron–ion model [1]:

$$S_{eI}(Q) = \frac{\rho(Q)}{\sqrt{Z_I}} S_{II}(Q) \tag{7}$$

$$\chi_{ee}(Q) = \frac{|\rho(Q)|^2}{Z_I} S_{II}(Q) + \frac{\chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0}. \tag{8}$$

Here, $\rho(Q)$ is the screening density distribution of a pseudo-atom defined by the non-interacting density response function χ_Q^0 and the direct correlation functions C_{ij} in the electron–ion mixture:

$$\rho(Q) \equiv \frac{n_0^e C_{eI}(Q) \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0}. \tag{9}$$

Thus, Eq. (7) leads to the exact relation, which must be followed in any electron–ion model:

$$Z_I S_{II}(0) = \sqrt{Z_I} S_{eI}(0) = S_{ee}(0) = \chi_{ee}(0) = n_0^e \kappa_T/\beta, \tag{10}$$

with the compressibility κ_T. By the inverse Fourier transform, the first part of the above equation is rewritten in the form

$$Z_I = n_0^e \int [g_{eI}(r) - 1] d\mathbf{r} - Z_I n_0^I \int [g_{II}(r) - 1] d\mathbf{r}, \tag{11}$$

which states that an ion fixed at the origin keeps the charge neutrality by accumulating the free electrons and by pushing away the ions around it in the whole space, not within the Wigner–Seitz cell.

On the other hand, when we fix an ion in the electron–ion mixure at the origin of coordinates, the nuclei forming this ion has the electron density $n_e(r)$ around it; this electron density $n_e(r)$ is obtained by solving a wave equation for the external potential caused by this fixed nucleus as a sum of the bound electron density $n_e^b(r)$ and the continuum electron density $n_e^c(r)$. Furthermore, the electron density $n_e(r)$ satisfies the following equation represented in terms of the Friedel sum of phase shifts $\delta\ell(E)$

$$\int [n_e(r) - n_0^e] d\mathbf{r} = \sum_{\varepsilon_i < 0} f(\varepsilon_i) + \frac{2}{\pi} \sum_\ell (2\ell + 1) \int_0^\infty f(E) \frac{d\delta_\ell(E)}{dE} dE, \tag{12}$$

where $n_e(r) = n_e^b(r) + n_e^c(r) = \rho_b(r) + n_e^f(r|N)$ is a sum of the "bound electron" distribution $\rho_b(r)$ and the free-electron distribution $n_e^f(r|N)$ with $f(\varepsilon) = 1/[\exp\{\beta(\varepsilon - \mu_e^0)\} + 1]$. If we take the bound-electron density $n_e^b(r)$ to define $Z_B = \int n_e^b(r) d\mathbf{r} = \sum_{\varepsilon_i<0} f(\varepsilon_i)$, the free-electron part $n_e^f(r) = n_e^c(r)$ must satisfy the following relation:

$$\begin{aligned} Z_I S_{II}(0) &= \int [n_e^f(r) - n_0^e] d\mathbf{r} = Z_I n_0^I \kappa_T/\beta \\ &= \frac{2}{\pi} \sum_\ell (2\ell + 1) \int_0^\infty f(E) \frac{d\delta_\ell(E)}{dE} dE. \end{aligned} \tag{13}$$

This relation is fulfilled generally for simple metals. However, there are some liquid metals and plasmas, for which this relation cannot be satisfied due to the large contribution of resonant phase-shifts and small compressibility κ_T at the high density. As a consequence, we must treat in general a part $\Delta\rho_b(r)$ of the continuum electron $n_e^c(r)$ as the part involved in the bound-electron distribution $\rho_b(r)$ to form an ion: $\rho_b(r) = n_e^b(r) + \Delta\rho_b(r)$ and $Z_B = \int [n_e^b(r) + \Delta\rho_b(r)] d\mathbf{r}$.

For the purpose of obtaining the expression of $\Delta\rho_b(r)$, we consider a chosen central ion as an atom immersed in the electron–ion mixture with a nucleus Z_A fixed at the origin of coordinates: the electron–ion model with a nucleus, forming the central ion, fixed at the origin is referred to as "the average atom (AA) model", hereafter. This nucleus accumulates electrons with the electron density $n_e(r) \equiv n_e(r|N)$ and pushes away surrounding ions with $n_I(r|N)$, keeping the charge neutrality condition around it:

$$Z_A = \int [n_e(r|N) - n_0^e] d\mathbf{r} - Z_I \int [n_I(r|N) - n_0^I] d\mathbf{r}. \tag{14}$$

The following three conditions are necessary for the electron density $n_e(r|N)$ to be consistent with the charge neutrality condition (11) in the electron–ion model.