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The average ion charge in the thermal ionization

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ABSTRACT

We show verification of our definition previously formulated for the average ion charge Z_I of plasmas and liquid metals in the electron-ion model for the case of the thermal ionization. For Rb plasmas of temperatures 5–30 eV and ion density $r_s^I = 5.388$, the form of the electron-ion radial distribution function (RDF) determined by the conventional method shows unphysical behavior just at the moment when the shallow 4d-bound level appears in the plasma state. However, according to our definition of the average ion charge, we show that such unphysical behavior in the RDF of Rb and H plasmas does not exist even at high temperature where the thermal ionization occur.

1. Introduction

The properties of matters such as plasmas or liquid metals have been investigated mainly by means of the density functional theory, and it has been a central subject especially to determine the equation of state (EOS) for wide range of temperature and density of matter. For the purpose of such investigation, we have addressed a theoretical treatment of plasmas or liquid metals employing the quantum hyper-netted (QHNC) method, where plasmas or liquid metals have been taken as a mixture of electrons and ions. However, the QHNC method has two problems to be improved; (1) establishing method to determine the ionic charge of matter, and (2) closing set of QHNC equations in self-consistent manner to determine the exchange part of the local field correction that is replaced the one for an electron gas in the jellium model, at present. For the first problem, it is apparently difficult to calculate a temperature dependence of the ionic charge in a hydrogen plasma, for example, due to lack of the established method to determine it so far.

As mentioned above, a liquid metal or a plasma can be taken as a mixture of electrons and ions of charge Z_I with electron density n_0^e and ion density n_0^I. In the case of liquid metal, we can obtain the value of the ionic charge Z_I involved implicitly in the structure factor by experiments, or obtain it employing the QHNC equation [1] if interparticle potentials $v_{ij}(r)$ are given. On the contrary, there are some difficulties to determine the ionic charge Z_I of plasma theoretically as well as hydrogen plasma. We already has shown how the ionic charge Z_I in a plasma must be defined in the frame work of the electron-ion model [2]. The purpose of this paper is to demonstrate validity of our definition of the ionic charge through examples of Rb and H plasmas in the thermal ionization.

2. Theory

Recently, we show the conditions to be satisfied in order to regard a plasma of pure matter with atomic number Z_A as the mixture of electron density n_0^e and ions of charge Z_I with density n_0^I (the electron-ion model) [2]:

$$Z_I = \frac{n_0^e}{n_0^I} = Z_A - \int \rho_b(r) d\boldsymbol{r}, \tag{1}$$

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

where the electron density $n_e(r)$ is the sum of bound and continuum electrons around an "average atom (AA)" with a nucleus Z_A fixed at the origin, $n_e(r) = n_e^b(r) + n_e^c(r)$: an ion in the electron-ion model is equated with an average atom in the AA model. The electron-ion RDF $g_{eI}(r)$ can be calculated with setting binary potentials $v_{ij}(r)$ to $v_{ee}(r) = 1/r, v_{II}(r) = Z_I^2/r$, and employing following form for $v_{eI}(r)$ [3]:

$$\begin{aligned} v_{eI}(r) \equiv & -\frac{Z_A}{r} + \int \frac{\rho_b(r')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' \\ & + \mu_{xc}\left(\rho_b(r) + n_0^e\right) - \mu_{xc}(n_0^e). \end{aligned} \tag{3}$$

The function μ_{xc} of the right-hand side of Eq. (3) is the exchange-correlation potential. The bound electron density distribution $\rho_b(r)$ defined as Eq. (2) gives the number of bound electrons by integrating

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as follows,

$$Z_B = \int \rho_b(r) d\mathbf{r}. \tag{4}$$

The potential $v_{eI}(r)$ of Eq. (3) is also interpreted as the potential $v_{eN}(r)$ between a nucleus fixed at origin and electrons around it, too. When $\rho_b(r)$ becomes consistent with both the electron-ion model and the AA model, $v_{eI}(r)$ is equal to $v_{eN}(r)$.

The difference $\Delta\rho(r)$ between $\rho_b(r)$ and bound electron distribution $n_e^b(r)$, $\Delta\rho(r) \equiv \rho(r) - n_e^b(r)$, gives the relation to determine the chemical potential μ_e^0 of the electron-ion mixture:

$$Z_A = \sum_{\varepsilon_i<0} \frac{1}{\exp[\beta(\varepsilon_i - \mu_e^0)] + 1} + \Delta Z_B + \frac{1}{n_0^I} \int \frac{2}{e^{\beta(p^2/2m - \mu_e^0)} + 1} \frac{d\mathbf{p}}{(2\pi\hbar)^3}, \tag{5}$$

where

$$\Delta Z_B \equiv \int \Delta\rho_b(r) d\mathbf{r}. \tag{6}$$

The quantity ΔZ_B comes from the resonance in the continuum (Eq. (3.87) in [1]), or from a part of the bound electrons $n_e^b(r)$, which does not contribute to the formation of an ion. For example, in a fully ionized hydrogen plasma, the bound electron distribution $\rho_b(r)$ is zero even though $n_b^e(r) \neq 0$, since the electron-proton radial distribution function (RDF) is given by $n_0^e g_{eI}(r) = n_e^b(r) + n_e^c(r)$ [4], that is,

$$\Delta Z_B = -\sum_{\varepsilon_i<0} \frac{1}{e^{\beta(\varepsilon_i - \mu_e^0)} + 1}. \tag{7}$$

In a simple metal on the other hand, there follows $\Delta Z_B = 0$, because of $Z_B = \int n_e^b(r) d\mathbf{r}$. However, if some new bound levels appear in consequence of raising the temperature of this simple metal, these new bound electrons cannot be recognized as real bound ones, but it is reasonable to understand that thermal ionization occurs (see Appendix B of Ref. [2]). So one must set the ΔZ_B as a sum of those thermal ionized electrons as follows,

$$\Delta Z_B = -\sum_{\varepsilon_i \in \text{thermal}} \frac{1}{e^{\beta(\varepsilon_i - \mu_e^0)} + 1}. \tag{8}$$

3. Results and conclusion

Next, we show the results of calculated radial distribution function (RDF) of Rb and H plasmas. In this calculation, we employ an electron gas in the jellium model to obtain the local field correction, which provides the exchange-correlation effect for the free electron density distribution $g_{eI}(r)$. On the other hand, the exchange-correlation of the bound electron density $\rho_b(r)$ is taken by the exchange-correlation potential $\mu_{xc}(\rho)$ of Gunnarsson and Lundqvist [5] for a zero temperature electron gas, since the bound electron density $\rho_b(r)$ is so dense as to be approximated as zero temperature. Then, the QHNC method with the combined use of Eqs. (1)–(6) provides numerical results for these matters. In this process, the Schrödinger equation is solved by Numerov's method; for bound states we used Herman–Skillman program [6].

Increasing temperature of liquid metals remaining same density of them, they become plasmas, and begin to yield thermal ionization (temperature localization) mentioned above. For example, a liquid metallic Rb is consist of Kr-like monovalent ions and free electrons. Raising the temperature of this liquid metallic Rb to become a plasma, new shallow 4d-bound level appears caused by thermal excitation from inner level in Rb ion. In an hydrogenoïd model the radius of the orbital of principal number n is $r_n \sim n^2 a_B / Z_{eff}$ where Z_{eff} is the effective charge of the nucleus; this may be estimated by $Z_{eff} \approx Z_A - \int n_e^b(r) d\mathbf{r}$, which is approximately equal to the ionization. So increasing the temperature increases the ionization and thus shrinks the atom leading to the appearance of new bound states.

If all bound electrons calculated are treated as bound electrons forming a Rb ion, the electron-ion RDF $g_{eI}(r)$ changes its shape discontinuously in the temperature region of the thermal ionization, where the 4d-bound level just appears in the Rb plasma [7]. However, in actual fact, this 4d-bound level is a part of free electrons to calculate the electron-ion RDF $g_{eI}(r)$, never to be included in $\rho_b(r)$ to form a Rb ion [8]:

$$\rho_b(r) = n_e^b(r) - n_e^{4d}(r), \tag{9}$$

$$n_0^e g_{eI}(r) = n_e^c(r) + n_e^{4d}(r), \tag{10}$$

then we must set $\Delta\rho(r)$ as

$$\Delta\rho(r) = -n_e^{4d}(r). \tag{11}$$

On our calculation, a Rb plasma already has shallow 4d-bound electron in the case of temperatures of 22 eV and 30 eV, but did not have that level at temperatures of 5 eV and 10 eV. In Table 1, we show the energies ε_i and occupation numbers $f(\varepsilon_i)$ of bound states in Rb plasma obtained by QHNC method for temperature 5 eV, 10 eV and 22 eV, where $f(\varepsilon_i)$ is a fermi function. Fig. 1 shows the obtained electron-ion RDFs $g_{eI}(r)$ of Rb plasma without (solid black line) or with (solid red line) 4d-bound electron density as core electrons at temperature 22 eV, and it also shows the electron-ion RDFs at $T = 5, 10$ eV (dashed blue lines) where no 4d bound level exist, and $T = 30$ eV(dashed black line). As shown in the Fig. 1, it is found that a peak of the electron-ion RDF with the 4d-bound electron density at $r \simeq 0.25 r_s^I$ is monotonically growing as increasing temperature $T = 5, 10, 22$ and 30 eV with the ion density $r_s^I = 5.388$. On the contrary, the RDF $g_{eI}(r)$ without the 4d-bound electron density of Rb plasma shrinks its shape in accordance with changing temperature of Rb plasma as 5 eV, 10 eV and 22 eV (solid red line in Fig. 1). Moreover, an ion involving shallow 4d-bound electron in Rb plasma becomes very large size (electron cloud size), therefore there is a case in which ions overlap to each other even outside of the average atomic sphere r_s^I, while the electron cloud does not overlap in the case the 4d-bound electron density $n_e^{4d}(r)$ is used to calculate $g_{eI}(r)$.

Perrot [9] showed the equation of state of Be plasmas considering them as liquid metals with high temperature: but this treatment includes the same problem about ionic charge state mentioned earlier in the text. Raising temperature of the liquid metallic Be, the shallow bound levels appear due to the thermal ionization. Perrot describes an ion so as to include a part of this shallow bound state to the bound electron density consisting of an ion. At higher temperatures for a certain range and with the more increased number of shallow bound levels, it becomes difficult to determine the charge Z_I of an ion of the Be plasmas. Therefore, the shallow bound electrons

Table 1
The energies (in Hartree) and occupation numbers $f(\varepsilon)$ of bound states in Rb plasma at temperature 5 eV, 10 eV and 22 eV, respectively. The ion charge Z_I for each temperature is also shown on the bottom row.

	5 eV		10 eV		22 eV	
	ε	$f(\varepsilon)$	ε	$f(\varepsilon)$	ε	$f(\varepsilon)$
3s	–21.00	1.00	–21.66	1.00	–23.26	1.00
3p	–16.31	1.00	–16.96	1.00	–18.56	1.00
3d	–7.81	1.00	–8.46	1.00	–10.06	0.98
4s	–2.14	0.99	–2.57	0.87	–3.55	0.50
4p	–1.02	0.84	–1.39	0.59	–2.28	0.31
4d	–		–		–0.35	0.12
Z_I	1.96		3.71		6.34	