

Dharma-wardana–Perrot theory and the quantal hypernetted-chain equation for strongly coupled plasmas

Junzo Chihara

Department of Physics, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan

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The Dharma-wardana and Perrot (DP) theory for a dense plasma is rewritten in another equivalent form in order to clarify its structure and approximations involved in it in comparison with the exact expression of structure factors in terms of the direct correlation functions (DCF) for a plasma as an ion-electron mixture. Thus it is shown that the DP theory breaks down when it treats a dense plasma with large bound-electron contribution, that is, with a significant number of bound electrons, as an ion. Also, this situation is numerically examined by using liquid metallic lithium as a test case, to which the quantal hypernetted-chain (QHNC) formulation is successfully applied. The breakdown in the DP theory is attributed to neglect of the electron-ion correlation given by the non-Coulomb part of the electron-ion DCF, $C_{ei}^{NC}(r)$, which is taken into account in the QHNC formulation. The non-Coulomb part $C_{ei}^{NC}(r)$ plays an important role in the reduction of a bare-electron-ion interaction $v_{ei}^C(r)$ to a weak pseudopotential, when a nucleus in a plasma begins to have core electrons forming an ion, since the DCF $C_{ei}(r) \equiv -\beta v_{ei}^C(r) + C_{ei}^{NC}(r)$ becomes a “weak” nonlinear pseudopotential $w_b^{NL}(r)$. Nevertheless, it turned out that one of the equations in the DP theory is useful to determine the nonlinear pseudopotential $w_b^{NL}(r)$ with use of the step-function approximation for the radial distribution $g_{II}(r)$ between ions. Recently Perrot, Furutani, and Dharma-wardana [Phys. Rev. A **41**, 1096 (1990)] tried to take account of the electron-ion correlation by using the QHNC approximation. However, it is shown that their improvement is not adequate to treat a plasma with core electrons in ions because of improper handling of the bound-electron density distribution in the definition of the electron-ion and electron-electron DCF's. From the comparison between the DP and QHNC approaches, a simplified method for treating a dense plasma is proposed to calculate a pseudopotential $w_b^{NL}(r)$, an effective interionic potential, and the electron-ion radial distribution function $g_{ei}(r)$, in addition to $g_{II}(r)$, with the use of the jellium-vacancy model.

I. INTRODUCTION

A plasma and a liquid metal are fundamentally a mixture of nuclei and electrons, in which interactions are clearly known as pure Coulombic potentials. Therefore, their properties in thermal equilibrium at a temperature $T = 1/k_B\beta$ and nucleus density n_0^I may be determined, in principle, only if the atomic number Z_A of a constituent nucleus is given as the only input data. However, it is a very difficult problem to treat a plasma in general from this standpoint, since this constitutes two coupled problems: one, to determine the internal structure of an ion in a plasma and the other, to calculate the external structure of ionic and electronic configurations in the space with use of a potential between these two “ions.” As a result, the atomic structure of an ion, the ion-electron configuration in the space, and the interionic potential must be determined to be all self-consistent in a plasma state, if we deal with a plasma as a nucleus-electron mixture. To this end, the density-functional theory [1–3] is a very useful and realistic approach, since it can treat classical and quantum fluids in a unified manner; in a plasma the electrons constitute a quantum liquid and the ions behaves as classical particles. On the basis of the density-functional theory, Dharma-wardana and Perrot

[4] (DP) derived a set of integral equations for static correlations in a strongly coupled plasma, and tried to obtain the various radial distribution functions in a hydrogen plasma by treating it as a coupled system of protons and electrons. On the other hand, a quantal version of the hypernetted-chain equation [5] (QHNC) was derived by using the density-functional method, and extended to treat a liquid metal and a plasma as an *ion*-electron mixture [6–8]. As a next step, the QHNC equation was generalized to be applicable to a liquid metal and a plasma as a *nucleus*-electron mixture [9]. At this stage, the QHNC formulation can determine the internal (atomic) and external (configurational) structures of a liquid metal and a plasma to be consistent with an interionic interaction between two “ions.” Its application to a liquid lithium [10] shows in comparison with the experiment that this formalism can successfully determine both the atomic [11] and configuration [10] structures in a self-consistent manner.

The DP theory was applied to various kind of problems: The determination of effective proton-proton interaction [12] and the examination of the onset of a bound state in a hydrogen plasma [13] were investigated. Also, optical properties [14,15] and electrical resistivity [16] in plasmas such as Fe and Xe were studied by this

formulation in addition to the calculation of the dynamical structure factors [17] of a hydrogen plasma. Furthermore, a method for calculating electric microfields in plasmas was proposed on the basis of the DP theory [18,19] and was applied to situations involving bound states, such as an aluminum immersed in a hydrogen plasma. Although there are many applications to various systems, as mentioned above, it is not yet clear what approximations are involved in the DP theory and what is the limitation of its applicability. Can this theory properly treat bound states to form an ion in a plasma? If it cannot deal with "ions," why can it not? It is already known that the DP theory ignores the electron-ion correlation in the effective potential acting ions and electrons around a fixed ion in a plasma [7,8,20], but it is not clear up to now what results from this neglect of the electron-ion correlation, which is taken into account in the QHNC formulation. Recently, Perrot, Furutani, and Dharma-wardana [20] (PFD) tried to improve the DP theory to take into account the electron-ion correlation by using the QHNC approximation. However, application of the PFD [20] and QHNC [8] methods to a hydrogen plasma shows only a significant but not drastic difference between the DP and these approaches, when the bound-electron contribution is small, that is, when hydrogens are almost perfectly ionized so that the ionic charge is $Z_I \approx Z_A$. Therefore, we attempt in the present article to examine how the bound-electron contribution is involved in the DP theory by taking liquid Li as a test case.

In Sec. II we rewrite the DP equation in order to clarify its structure and approximations in it on the basis of *exact* expressions for the structure factors in terms of the direct correlation functions for an ion-electron mixture: Some exact relations are summarized in the last part of Sec. II. In Sec. III the DP theory is examined numerically by comparing with the QHNC result for a liquid metallic lithium, which has a significant bound-electron contribution. Section IV is devoted to a concluding discussion, where the recent work of PFD is also criticized.

II. THE DP THEORY

The radial distribution functions $g_{II}(r)$ and $g_{eI}(r)$, concerning ions and electrons are identical with the inhomogeneous ion and free-electron density distributions $n_I(r)/n_0^I$ and $n_e^f(r)/n_0^e$, around a fixed nucleus with a charge Z_A in a plasma of uniform ion density n_0^I and electron density n_0^e , respectively. It should be kept in mind that the total electron density distribution $n_e(r)$ around the nucleus is assumed to be clearly divided into the free- and bound-electron density distributions; the former $n_e^f(r)$ is taken as the radial distribution function (RDF) between electron and ion, and the latter $n_e^b(r)$ constitutes an ion in a plasma as an ion-electron mixture. In the DP theory [4], the effective potentials for electrons and ions caused by a fixed nucleus in a plasma are written as follows:

$$V_I(r) = Z_I \left[\frac{Z_A}{r} + V_P(r) \right] - \frac{1}{\beta} n_0^I \int [h(r') - \ln g_{II}(r')] h(|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}', \quad (1)$$

$$V_e(r) = - \left[\frac{Z_A}{r} + V_P(r) \right] + \mu_{XC}(n_e(r)) - \mu_{XC}(n_0^e), \quad (2)$$

where

$$V_P(r) \equiv \int v_{ee}^c(|\mathbf{r}-\mathbf{r}'|) [Z_I n_I(r') - n_e(r')] d\mathbf{r}' \quad (3)$$

and $h(r) \equiv g_{II}(r) - 1$; Z_I is the ionic valency. Here, $\mu_{XC}(n_e(r))$ denotes the exchange-correlation potential and $v_{ij}^c(r)$ is the pure Coulomb potential between i - j particles. These effective potentials caused by the nucleus are rewritten in the forms

$$V_I(r) = \bar{v}_{II}(r) - \Gamma_{II}^{\text{DP}}(r)/\beta, \quad (4)$$

$$V_e(r) = \bar{v}_{eI}(r) - \Gamma_{eI}^{\text{DP}}(r)/\beta, \quad (5)$$

with the definition of a bare ion-ion and electron-ion interactions,

$$\bar{v}_{II}(r) \equiv Z_I \left[\frac{Z_A}{r} - \int v_{ee}^c(|\mathbf{r}-\mathbf{r}'|) n_e^b(r') d\mathbf{r}' \right], \quad (6)$$

$$\bar{v}_{eI}(r) \equiv - \frac{Z_A}{r} + \int v_{ee}^c(|\mathbf{r}-\mathbf{r}'|) n_e^b(r') d\mathbf{r}' + \mu_{XC}(n_e^b(r) + n_0^e) - \mu_{XC}(n_0^e). \quad (7)$$

In the above, two functions $\Gamma_{II}^{\text{DP}}(r)$ and $\Gamma_{eI}^{\text{DP}}(r)$ are defined by

$$\begin{aligned} \Gamma_{II}^{\text{DP}}(r)/\beta &\equiv - \int v_{ee}^c(|\mathbf{r}-\mathbf{r}'|) \delta n_e^f(r') d\mathbf{r}' \\ &\quad - \int v_{II}^c(|\mathbf{r}-\mathbf{r}'|) n_0^I h(r') d\mathbf{r}' \\ &\quad + \frac{1}{\beta} n_0^I \int [h(r') - \ln g_{II}(r')] h(|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}', \end{aligned} \quad (8)$$

$$\begin{aligned} \Gamma_{eI}^{\text{DP}}(r)/\beta &\equiv \int \frac{C_{ee}^{\text{DP}}(|\mathbf{r}-\mathbf{r}'|)}{\beta} \delta n_e^f(r') d\mathbf{r}' \\ &\quad - \int v_{eI}^c(|\mathbf{r}-\mathbf{r}'|) n_0^I h(r') d\mathbf{r}', \end{aligned} \quad (9)$$

with

$$\delta n_e^f(r) \equiv n_e^f(r) - n_0^e = n_0^e g_{eI}(r) - n_0^e$$

and

$$C_{ee}^{\text{DP}}(r) \equiv C_{ee}^{\text{XC,DP}}(r) - \beta v_{ee}^c(r). \quad (10)$$

Here, $C_{ee}^{\text{XC,DP}}$ is the exchange-correlation factor defined by

$$\begin{aligned} &\int \frac{C_{ee}^{\text{XC,DP}}(|\mathbf{r}-\mathbf{r}'|)}{-\beta} \delta n_e^f(r') d\mathbf{r}' \\ &\equiv \mu_{XC}(n_e^f(r) + n_e^b(r)) - \mu_{XC}(n_0^e + n_e^b(r)) \\ &\approx \mu_{XC}(n_e^f(r)) - \mu_{XC}(n_0^e) \end{aligned}$$

for outside the core region, (11)

which is regarded as representing the exchange-correlation potential caused by free electrons in the total exchange-correlation potential $W_e^{ee}(r)$:

$$\begin{aligned} W_e^{ee}(r) &\equiv \mu_{XC}(n_e(r)) - \mu_{XC}(n_0^e) \\ &= \mu_{XC}(n_e^b(r) + n_0^e) - \mu_{XC}(n_0^e) \\ &\quad + \mu_{XC}(n_e(r)) - \mu_{XC}(n_e^b(r) + n_0^e). \end{aligned} \quad (12)$$

Remember that the first and second terms in the above equation are taken to constitute a bare electron-ion interaction (7). At this stage, we introduce two further new functions $C_{II}^{DP}(r)$ and $C_{eI}^{DP}(r)$, which are expected to play the role of the direct correlation functions (DCF's) in the QHNC equation:

$$C_{II}^{DP}(r) \equiv \exp[-\beta \bar{v}_{II}(r) + \Gamma_{II}^{DP}(r)] - 1 - \Gamma_{II}^{DP}(r), \quad (13)$$

$$\hat{B}C_{eI}^{DP}(r) \equiv n_e^{of}(r) |\bar{v}_{eI} - \Gamma_{eI}^{DP}/\beta| / n_0^e - 1 - \hat{B}\Gamma_{eI}^{DP}(r), \quad (14)$$

where \hat{B} denotes an operator defined by

$$\begin{aligned} \mathcal{F}_Q[\hat{B}^\alpha f(r)] &\equiv (\chi_Q^0)^\alpha \mathcal{F}_Q[f(r)] \\ &= (\chi_Q^0)^\alpha \int e^{i\mathbf{Q}\cdot\mathbf{r}} f(r) d\mathbf{r} \end{aligned} \quad (15)$$

for an arbitrary real number α , and χ_Q^0 denotes the density response function of the noninteracting system. Then, Eq. (8) is rewritten in a simple form in terms of $C_{II}^{DP}(r)$:

$$\begin{aligned} \Gamma_{II}^{DP}(r) &= -\beta \int v_{ie}^c(|\mathbf{r} - \mathbf{r}'|) \delta n_e^f(\mathbf{r}') d\mathbf{r}' \\ &\quad + \int C_{II}^{DP}(|\mathbf{r} - \mathbf{r}'|) n_0^I h(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (16)$$

Finally, the RDF's in the DP theory are written in the forms

$$g_{II}(r) = \exp[-\beta \bar{v}_{II}(r) + \Gamma_{II}^{DP}(r)], \quad (17)$$

$$g_{eI}(r) = n_e^{of}(r) |\bar{v}_{eI} - \Gamma_{eI}^{DP}/\beta| / n_0^e, \quad (18)$$

where $n_e^{of}(r|V_e)$ is the free-electron part of the electron density

$$\begin{aligned} n_e(r) &= n_e^0(r|V_e) \equiv n_e^{ob}(r|V_e) + n_e^{of}(r|V_e) \\ &= n_e^b(r) + n_e^f(r), \end{aligned}$$

which is determined by solving the wave equation for an electron under the external potential $V_e(r)$. Then, Eqs. (13) and (14) are written in forms analogous to the Ornstein-Zernike (OZ) equations in the QHNC formulation, as will be described later:

$$g_{II}(r) - 1 = C_{II}^{DP}(r) + \Gamma_{II}^{DP}(r), \quad (19)$$

$$g_{eI}(r) - 1 = \hat{B}C_{eI}^{DP}(r) + \hat{B}\Gamma_{eI}^{DP}(r). \quad (20)$$

The structure factors in the DP theory are obtained in terms of $C_{II}^{DP}(Q)$, $C_{eI}^{DP}(Q)$, and $C_{ee}^{DP}(Q)$ by the Fourier transforms of Eqs. (19) and (20) in the forms

$$S_{II}(Q) = \frac{1}{D'(Q)} \begin{vmatrix} 1, & \sqrt{n_0^I n_0^e} \beta v_{ie}^c(Q) \\ A(Q), & 1 - n_0^e C_{ee}^{DP}(Q) \chi_Q^0 \end{vmatrix}, \quad (21)$$

$$S_{eI}(Q) = \frac{1}{D'(Q)} \begin{vmatrix} 1 - n_0^I C_{II}^{DP}(Q), & 1 \\ \sqrt{n_0^I n_0^e} \beta v_{eI}^c(Q) \chi_Q^0, & A(Q) \end{vmatrix} \quad (22)$$

$$= \frac{\rho_{DP}(Q)}{\sqrt{Z_I}} S_{II}(Q), \quad (23)$$

where

$$D'(Q) \equiv \begin{vmatrix} 1 - n_0^I C_{II}^{DP}(Q), & \sqrt{n_0^I n_0^e} \beta v_{ie}^c(Q) \\ \sqrt{n_0^I n_0^e} \beta v_{eI}^c(Q) \chi_Q^0, & 1 - n_0^e C_{ee}^{DP}(Q) \chi_Q^0 \end{vmatrix}, \quad (24)$$

$$\rho_{DP}(Q) \equiv \frac{-n_0^e \beta v_{eI}^c(Q) \chi_Q^0 + A(Q) \sqrt{Z_I} [1 - n_0^I C_{II}^{DP}(Q)]}{1 - n_0^e C_{ee}^{DP}(Q) \chi_Q^0 - A'(Q)}, \quad (25)$$

$$A(Q) \equiv \sqrt{n_0^I n_0^e} \chi_Q^0 [C_{eI}^{DP}(Q) + \beta v_{eI}^c(Q)], \quad (26)$$

$$A'(Q) \equiv \sqrt{n_0^I n_0^e} \beta v_{eI}^c(Q) A(Q). \quad (27)$$

We can think of a plasma consisting of ions and electrons as a one-component fluid interacting via an effective interatomic potential $v^{\text{eff}}(r)$, which yields the same RDF to $g_{II}(r)$ in the ion-electron mixture. In the DP theory, this effective potential is proved to be expressed in terms of $C_{eI}^{DP}(Q)$ and $C_{II}^{DP}(Q)$ by following the similar procedure [21] to define $v^{\text{eff}}(r)$ in the QHNC equation:

$$\begin{aligned} \beta v^{\text{eff}}(Q) &= \beta \bar{v}_{II}(Q) \\ &\quad - \frac{|\beta v_{eI}(Q)|^2 n_0^e \chi_Q^0 - [1 - n_0^I C_{II}^{DP}(Q)] A'(Q) / n_0^I}{1 - n_0^e C_{ee}^{DP}(Q) \chi_Q^0 - A'(Q)} \end{aligned} \quad (28)$$

$$= \beta \bar{v}_{II}(Q) + \beta v_{eI}^c(Q) \rho_{DP}(Q). \quad (29)$$

On the other hand, in the QHNC formulation [3,8], the structure factors for a plasma as an ion-electron mixture are written in terms of the DCF's $C_{ij}(Q)$,

$$S_{II}(Q) = [1 - n_0^e C_{ee}(Q) \chi_Q^0] / D(Q), \quad (30)$$

$$S_{eI}(Q) = \sqrt{n_0^I n_0^e} C_{eI}(Q) \chi_Q^0 / D(Q) \quad (31)$$

$$= \frac{\rho(Q)}{\sqrt{Z_I}} S_{II}(Q), \quad (32)$$

where

$$\rho(Q) \equiv \frac{n_0^e C_{eI}(Q) \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0}, \quad (33)$$

$$\begin{aligned} D(Q) &\equiv [1 - n_0^I C_{II}(Q)] [1 - n_0^e C_{ee}(Q) \chi_Q^0] \\ &\quad - n_0^I n_0^e |C_{eI}(Q)|^2 \chi_Q^0. \end{aligned} \quad (34)$$

The OZ relations for the ion-electron mixture are obtained from the inverse Fourier transforms of the above equations as

$$g_{II}(r) - 1 = C_{II}(r) + \Gamma_{II}(r), \quad (35)$$

$$g_{eI}(r) - 1 = \hat{B}C_{eI}(r) + \hat{B}\Gamma_{eI}(r), \quad (36)$$

where

$$\Gamma_{II}(r) \equiv \int C_{Ie}(|\mathbf{r}-\mathbf{r}'|) n_0^e [g_{eI}(r') - 1] d\mathbf{r}' + \int C_{II}(|\mathbf{r}-\mathbf{r}'|) n_0^I h(r') d\mathbf{r}', \quad (37)$$

$$\Gamma_{eI}(r) \equiv \int C_{ee}(|\mathbf{r}-\mathbf{r}'|) n_0^e [g_{eI}(r') - 1] d\mathbf{r}' + \int C_{eI}(|\mathbf{r}-\mathbf{r}'|) n_0^I h(r') d\mathbf{r}'. \quad (38)$$

At this point, it should be noted that Eqs. (30)–(38) are *exact* expressions, provided that a plasma can be regarded as an ion-electron mixture and that the ions in a plasma behave as classical particles. The above equations are derived only by the definition of the DCF's for the ion-electron mixture [3]:

$$C_{ij}(|\mathbf{r}-\mathbf{r}'|) \equiv -\beta \frac{\delta^2 F_{\text{int}}[n_f, n_e]}{\delta n_i(\mathbf{r}) \delta n_j(\mathbf{r}')} \Big|_0, \quad (39)$$

which means the functional derivative of the interaction part of intrinsic free energy F_{int} at the uniform densities. In this connection, the RDF's have been derived previously by thinking of a plasma as a nucleus-electron mixture [9]:

$$g_{II}(r) = \exp[-\beta v_{II}^c(r) + \Gamma_{II}(r) + B_{II}(r)], \quad (40)$$

$$g_{eI}(r) = n_0^{eI}(r) \bar{v}_{eI} - \Gamma_{eI} / \beta / n_0^e. \quad (41)$$

Therefore, Eqs. (40) and (41) coupled with the OZ relations (35) and (36) constitute a closed set of integral equations [10] for $C_{II}(r)$ and $C_{eI}(r)$, which are written in the same forms to Eqs. (13) and (14), if the bridge function $B_{II}(r)$ and the DCF $C_{ee}(r)$ are given beforehand.

In the QHNC formulation [9,10] the number of bound electrons forming an ion in a plasma is defined by $Z_B = \int_0^\infty n_e^b(r) d\mathbf{r}$ in terms of the bound-electron distribution $n_e^b(r)$ obtained from the one-center Schrödinger equation for the potential $\bar{v}_{eI}(r) - \Gamma_{eI}(r)/\beta$. In other words, the effective ionic charge Z_I is defined by $Z_I \equiv Z_A - Z_B$, that is,

$$Z_I \equiv Z_A - \sum_{\epsilon_i < 0} \frac{1}{\exp(\beta \epsilon_i - \mu_e^0) + 1}, \quad (42)$$

with a chemical potential μ_e^0 determined by

$$\lim_{r \rightarrow \infty} n_e^f(r) = \int \frac{2}{\exp(\beta p^2/2m - \mu_e^0) + 1} \frac{d\mathbf{p}}{(2\pi)^3} = n_0^e = Z_I n_0^I. \quad (43)$$

The effective interatomic potential [21] in the QHNC formulation is exactly represented by

$$\beta v^{\text{eff}}(Q) \equiv \beta v_{II}^c(Q) - \frac{|C_{eI}(Q)|^2 n_0^e \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0} \quad (44)$$

$$= \beta v_{II}^c(Q) - C_{eI}(Q) \rho(Q), \quad (45)$$

if the bridge function of the equivalent one-component fluid is chosen to be equal with the bridge function $B_{II}(r)$ of the ion-electron mixture.

III. COMPARISON BETWEEN THE DP AND QHNC EQUATIONS

Recently, we have applied the QHNC formulation to a liquid metallic lithium [10] and obtained structure factors $S_{II}(Q)$ at two temperatures, which show excellent agreement with the experimental ones [22]. A liquid metal is considered as one kind of a strongly coupled plasma, if a plasma can be taken to consist of ions and electrons. Therefore, an application of a formulation determining the structure of a plasma to a liquid metal offers a severe test for its validity, since there are a great deal of reliable experiments in liquid metals. A lithium atom in a liquid metal has two 1s electrons and one valence electron; the electron-ion correlation arising from bound electrons is strong in comparison with a hydrogen plasma. So we consider here the limitation of validity in the DP theory by taking the case of a liquid metal Li. Here, we introduce the following two approximations in the DP equation. The bare ion-ion interaction potential defined by Eq. (6) can be approximated as

$$\bar{v}_{II}(r) = Z_I \left[\frac{\left[Z_A - \int_0^r n_e^b(r') d\mathbf{r}' \right]}{r} - \int_r^\infty \frac{n_e^b(r')}{r'} d\mathbf{r}' \right] \approx \frac{Z_I^2}{r} = v_{II}^c(r), \quad (46)$$

since the bound-electron core in a lithium ion is small and rigid enough. Second, the factor $C_{ee}^{\text{XC,DP}}(Q)$ representing the exchange-correlation effect due to the free electrons is taken to be expressed by the local-field correction (LFC) $G(Q)$ of the jellium model, as follows:

$$C_{ee}^{\text{XC,DP}}(Q) \approx \beta v_{ee}^c(Q) G(Q). \quad (47)$$

Then, the expression $\chi_Q^0 / [1 - n_0^e C_{ee}^{\text{DP}}(Q) \chi_Q^0]$ reduces to the density-density response function χ_Q^{Jell} of the electron gas in the jellium model. At this point, it should be noted that in the DP theory there is no concept of an "ion" as is ascertained from Eq. (2), since it cannot be divided into the core-electron and free-electron parts to set up an electron-"ion" interaction $\bar{v}_{eI}(r)$. Therefore, the approximation (47) brings about "ions" in the DP theory, since $C_{ee}^{\text{XC,DP}}(Q)$ becomes now independent of the bound-electron distribution, and represents the exchange-correlation effect between free electrons.

If the bridge function $B_{II}(r)$ is added to Eq. (5) in addition to the approximations (46) and (47), the DP theory becomes identical with the QHNC formulation except that the DCF $C_{eI}(r)$ in Eqs. (37) and (38) are replaced by $-\beta v_{eI}^c(r)$; we investigate below what results from this difference. In the QHNC approach based on the nucleus-electron model where the density-functional theory is applied to a single-center problem to determine density distributions around a fixed nucleus, the expressions for the bare electron-ion interaction $\bar{v}_{eI}(r)$ and the ionic charge Z_I are obtained by (7) and (42), respectively, but the bare ion-ion interaction $v_{II}(r)$ remains undetermined: The ion-ion interaction is assumed here to be a pure Coulombic potential between two ions. This ap-

proximation is only valid when the overlap of core electrons is small. In addition, the ionic charge is simply defined in terms of the number of electrons belonging to the clearly defined bound states: Thus, resonant states cannot be treated in this formalism. Therefore, applicability of the QHNC and modified DP approaches are limited to "simple metallic" systems where the overlap of core electrons and the resonant states is negligible. In the numerical calculation, we use the Hubbard-Geldart-Vosko form [23] for $G(Q)$ and the Gunnarson-Lundqvist approximation [24] for the exchange-correlation potential $\mu_{XC}(n_e(r))$. Also, the bridge function $B_{II}(r)$ in Eq. (40) is taken to be that of the Percus-Yevick equation for the hard spheres specified by the packing fraction η , as was done in the modified HNC equation [25].

As a first step, we try to examine the approximation involved in the factor $\rho_{DP}(Q)$ of Eq. (25) in the DP theory. The free-electron distribution $n_e^0 g_{el}(r)$ around the fixed ion in a plasma can be regarded as the superposition of surrounding "neutral pseudoatoms," each of which carries about a screening cloud $\rho(r)$ in such a way as is described by the following exact equation:

$$n_e^0 g_{el}(r) = \rho(r) + n_0^I \int \rho(|\mathbf{r}-\mathbf{r}'|) g_{II}(r') \mathbf{r}', \quad (48)$$

which results from the inverse Fourier transform of Eq. (32). For a liquid Li at 470 K, a screening cloud $\rho(r)$ and a total screening cloud $\rho_{PA}(r)$ of a pseudoatom calculated by the QHNC equation are exhibited in Fig. 1 along with

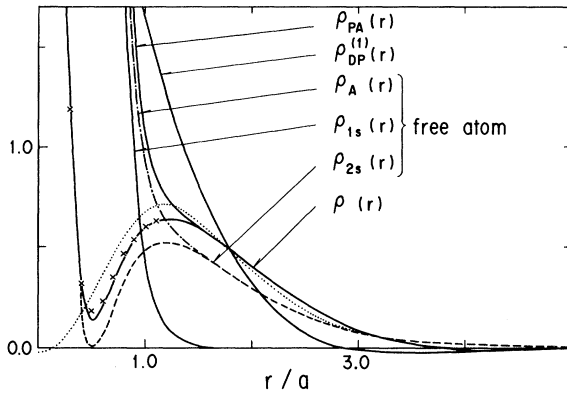


FIG. 1. Screening clouds of a neutral pseudoatom in a liquid metal lithium at 470 K calculated by various approximations in comparison with the QHNC result denoted by $\rho(r)$, which shows similar behavior to the density distribution $\rho_{2s}(r)$ of a free lithium atom. The curve of $\rho_{DP}^{(1)}(r)$ is a simple linear response density to a bare Coulomb potential, which contains some contribution of the bound-electron density as the total densities $\rho_A(r)$ and $\rho_{PA}(r)$, of free and pseudoatoms. The $1s$ electron density distribution $n_e^b(r)$ of the pseudoatom coincides with $\rho_{1s}(r)$ of the free atom. The crosses display the density $\rho_{DP}^{(0)}(r)$ based on the jellium-vacancy model, while the dotted curve denotes the linear response density with the use of the Ashcroft pseudopotential. Here, density distributions are normalized by the uniform density n_0^0 , and the distance r in units of $a \equiv (3/4\pi n_0^I)^{1/3}$.

the $1s$ electron density distribution $\rho_{1s}(r)$ of a free lithium atom, which coincides with the bound-electron density distribution $n_e^b(r)$ calculated by the QHNC equation. Here, in addition to Eqs. (46) and (47), we introduce the random-phase approximation (RPA)

$$C_{el}^{DP}(Q) \approx -\beta v_{el}^C(Q), \quad (49)$$

which reduces Eq. (25) to a simple expression,

$$\rho_{DP}(Q) \approx \rho_{DP}^{(1)}(Q) \equiv -n_0^0 \beta v_{el}^C(Q) \chi_Q^{jell}. \quad (50)$$

This expression means that $\rho_{DP}(Q)$ in the RPA becomes the linear response density $\rho_{DP}^{(1)}(Q)$ to a disturbance potential $v_{el}^C(Q)$ in the uniform electron gas. It should be noted that the linear response density $\rho_{DP}^{(1)}(Q)$ contains some contribution of the bound-electron density distribution as shown in Fig. 1, where we can see that $\rho_{DP}^{(1)}(r)$ is very large in the core region similarly to the total electron density distribution $\rho_A(r)$ of a free Li atom. From this fact, the electron cloud $\rho_{DP}(Q)$ is considered to involve the bound-electron contribution to some extent, since $\rho_{DP}(Q)$ given by Eq. (25) has essentially the same structure as $\rho_{DP}^{(1)}(Q)$. On the other hand, the electron cloud in the pseudopotential theory is given by

$$\rho(Q) = -n_0^0 \beta w_b(Q) \chi_Q^{jell}, \quad (51)$$

which takes the same linear response expression as $\rho_{DP}^{(1)}(Q)$ except that the bare Coulomb potential $v_{el}^C(Q)$ is replaced by the pseudopotential $w_b(Q)$. Due to the pseudopotential $w_b(Q)$, Eq. (51) does not contain the bound-electron contribution as is shown in Fig. 1, where the cloud $\rho(r)$ calculated by the QHNC equation is also shown to exclude the bound-electron density and to exhibit a behavior quite similar to $2s$ electron density $\rho_{2s}(r)$ in a free Li atom. Here, the calculation of Eq. (51) is made by the use of the Ashcroft model potential with the core radius $r_c = 0.74 \text{ \AA}$. The comparison of $\rho_{DP}^{(1)}(r)$ with the QHNC and model-potential results suggests that the DP theory breaks down when the bound-electron contribution becomes significant, since their expression for $\rho_{DP}(Q)$ in Eq. (25) contains the bare Coulomb potential $v_{el}^C(Q)$. For the same reason, the effective interionic interaction given by Eq. (28) becomes invalid when the bound-electron contribution becomes large, because it reduces to

$$\beta v^{eff}(Q) \approx \beta v_{II}^C(Q) - |\beta v_{el}^C(Q)|^2 n_0^0 \chi_Q^{jell} \quad (52)$$

in the RP approximation.

Next, we obtain a criterion that the limitation of applicability in the DP theory is as follows. The zero-wave-number limit of $S_{II}(Q)$ in the DP equation results in

$$\lim_{Q \rightarrow 0} S_{II}(Q) = \frac{n_0^I \kappa'}{\beta} (1 - \gamma), \quad (53)$$

where

$$\frac{\beta}{n_0^I \kappa'} \equiv 1 + \frac{2}{3} \beta E_F - n_0^I C_{II}^{DP}(0) - Z_I^2 n_0^I C_{ee}^{DP}(0), \quad (54)$$

$$\gamma \equiv - \lim_{Q \rightarrow 0} n_0^0 [C_{el}^{DP}(Q) + \beta v_{el}^C(Q)], \quad (55)$$

while the QHNC equation gives this limit [26]

$$\lim_{Q \rightarrow 0} S_{II}(Q) = \frac{n_0^I \kappa}{\beta}, \quad (56)$$

with

$$\begin{aligned} \frac{\beta}{n_0^I \kappa} \equiv & 1 + \frac{2}{3} \beta E_F - n_0^I C'_{II}(0) - Z_I^2 n_0^I C'_{ee}(0) \\ & - 2Z_I n_0^I C'_{eI}(0). \end{aligned} \quad (57)$$

In the above, the dashed C'_{ij} 's denote the non-Coulomb parts of C_{ij} 's in the DP and QHNC expressions, respectively, and E_F is the Fermi energy, which gives the Bohm-Staver term in the compressibility formula (57). Since the compressibility must be positive, we obtain the condition that $1 - \gamma > 0$ and $\kappa' > 0$ for the DP theory to be valid. Hence, we can state that the bound-electron contribution in the DP theory is small when $\gamma \ll 1$. The value of γ for a liquid Li can be estimated by

$$\gamma = 3Z_I \Gamma x_c^2, \quad (58)$$

which is obtained if $C_{eI}^{DP}(Q)$ in Eq. (55) is approximated by the Ashcroft model potential $-\beta w_b(Q)$ with $x_c \equiv r_c / (r_s a_B)$ in units of the Bohr radius a_B . This relation yields $\gamma = 109$ for a liquid Li at 470 K. On the other hand, the value of γ with use of $C_{eI}^{DP}(Q)$ obtained by the numerical method, as will be mentioned, is 91, which indicates that Eq. (58) gives a good estimation. Thus, we have shown that the DP theory cannot be applied to a liquid metal, where the bound-electron contribution is very important, as shown by $\gamma = 91 \gg 1$ for a liquid lithium.

In this connection, we investigate the problem where this breakdown in the DP theory comes from, if applied to a liquid metal, which is a typical system of an ion-electron mixture with a significant bound-electron contribution, that is, with $Z_I \ll Z_A$. The RDF's, $g_{II}(r)$ and $g_{eI}(r)$, in the DP theory are determined by the coupled equations (13) and (14). The equation for $C_{eI}^{DP}(r)$ [or $g_{eI}(r)$] given by Eq. (14) is insensitive to the approximate RDF $g_{II}(r)$ involved in $\Gamma_{eI}^{DP}(r)$. On the contrary, the RDF $g_{II}(r)$ determined by Eq. (13) is quite sensitive to the error in the RDF $g_{eI}(r)$ contained in $\Gamma_{II}^{DP}(r)$, as will shown later.

In the first place, we show that the second equation (14) of the DP theory can afford to give $C_{eI}^{DP}(r)$ as a good approximation to the DCF $C_{eI}(r)$, which plays the role of a nonlinear pseudopotential [3,10] to determine the effective interionic potential (44), and yields a fairly good but not sufficiently accurate $g_{eI}(r)$ to be used in the first equation (13) to determine $g_{II}(r)$. It should be noted that the second equation (14) can determine $C_{eI}^{DP}(r)$ [or $g_{eI}(r)$] without use of Eq. (13), provided that the RDF $g_{II}(r)$ is given beforehand. Here, we approximate $g_{II}(r)$ involved in $\Gamma_{eI}^{DP}(r)$ by the step function $\theta(r - R_{WS})$ with the Wigner-Seitz radius R_{WS} ,

$$g_{II}(r) \approx \Theta(r - R_{WS}). \quad (59)$$

This approximation reduces the determination of $g_{eI}(r)$

in the ion-electron mixture to the problem to calculate the electron density $n_e(r) = n_e^f(r) + n_e^b(r)$ in the jellium-vacancy model, since the effective potential $V_e(r)$ given by Eq. (2) becomes

$$\begin{aligned} V_e(r) = & -\frac{Z_A}{r} + \int v_{ee}^C(|\mathbf{r} - \mathbf{r}'|) [n_e(r') \\ & - n_0^e \Theta(r' - R_{WS})] d\mathbf{r}' \\ & + \mu_{XC}(n_e(r)) - \mu_{XC}(n_0^e), \end{aligned} \quad (60)$$

which represents a potential caused by a fixed nucleus at the center of a vacancy in the jellium model. This procedure is equivalent to the method to determine the nonlinear pseudopotential as proposed by Dagens, Rasolt, and Taylor [27] (DRT) and Manninen *et al.* [28]. The Fourier transform of the OZ-like equation (20) with (9) leads to the relation

$$S_{eI}(Q) = \rho_{DP}^{(0)}(Q) + \rho_{DP}^{(1)}(Q) [S_{II}(Q) - 1], \quad (61)$$

with

$$\rho_{DP}^{(0)}(Q) \equiv n_0^e C_{eI}^{DP}(Q) \chi_Q^{jell} \quad (62)$$

and $\rho_{DP}^{(1)}(Q)$ defined by Eq. (50). The step-function approximation for $g_{II}(r)$ alters the above equation in the form

$$S_{eI}(Q) = \rho_{DP}^{(0)}(Q) - n_0^e v_{eI}^C(Q) \beta \nu(Q) \beta \chi_Q^{jell}, \quad (63)$$

where

$$\nu(Q) = n_0^I \mathcal{F}_Q [\Theta(r - R_{WS}) - 1]. \quad (64)$$

This equation enables us to obtain $\rho_{DP}^{(0)}(Q)$, once the RDF $g_{eI}(r)$ is determined by solving the wave equation for an electron under the external potential (60), since the second term of Eq. (63) is now represented by known functions. From $\rho_{DP}^{(0)}(Q)$ with use of Eq. (62), we can obtain $-C_{eI}^{DP}(Q)/\beta$, which plays the role of nonlinear pseudopotential, since this procedure is essentially the same as the determination of the nonlinear pseudopotential by DRT. In this way, we calculate $-C_{eI}^{DP}(r)/\beta$ for a liquid Li at temperature 470 K, with use of the approximations (59) and (47), and the result is shown by the crosses in Fig. 2, where the nonlinear pseudopotential $w_e^{NL}(r) = -C_{eI}(r)/\beta$ calculated by the QHNC equation and the Ashcroft model potential with $r_c = 0.74 \text{ \AA}$ are plotted by the solid and the dashed curves, respectively, for comparison. The circles in Fig. 2 denote $w_e^{NL}(r) = -C_{eI}(r)/\beta$ obtained by the QHNC equation (41) with use of the step-function approximation for $g_{II}(r)$ in Eq. (38). On the other hand, the screening cloud $\rho_{DP}^{(0)}(r)$ obtained in this way is exhibited in Fig. 1 by the crosses, which shows a good agreement with the QHNC result as well as $C_{eI}^{DP}(r)$ in Fig. 2, although the step-function approximation to $g_{II}(r)$ is quite a crude one. This fact shows that Eq. (14) is insensitive to the RDF $g_{II}(r)$ involved in $\Gamma_{eI}^{DP}(r)$, and that it determines $C_{eI}^{DP}(r)$ and $\rho_{DP}^{(0)}(r)$ in an excellent agreement with the QHNC results, although the electron-ion correlation is neglected in $\Gamma_{eI}^{DP}(r)$. In other words, the second equation (14) of the

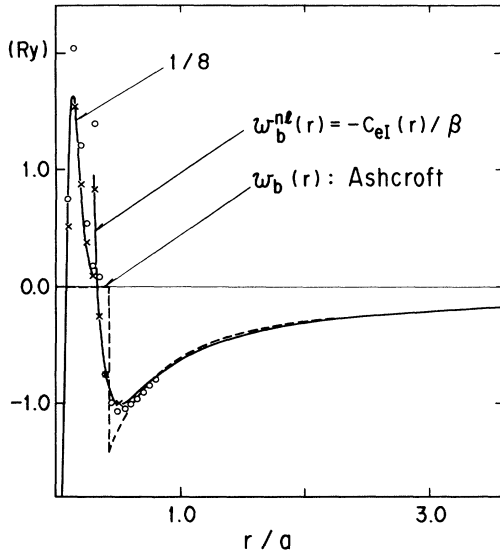


FIG. 2. Nonlinear pseudopotentials $w_b^{NL}(r)$ calculated in terms of electron-ion DCF's with various approximations. The solid curve is that of the full QHNC calculation, while the crosses and white circles denote those of the DP and QHNC equations using the step-function approximation for $g_{II}(r)$, respectively. The Ashcroft model potential is shown by the dashed curves. Near the origin, $w_b^{NL}(r)$'s are displayed in the reduced scale with $\frac{1}{8}$.

DP theory may provide an accurate formula to determine the nonlinear pseudopotential $w_b^{NL}(r) = -C_{eI}(r)/\beta$, which is equivalent in essence to the DRT procedure. At this point it is interesting to note that this equation provides the pseudopotential for a plasma at arbitrary temperature and density. Also, it should be emphasized that the RDF $g_{eI}(r)$ in the definition of the function $C_{eI}^{DP}(r)$ by Eq. (14) does not involve the bound-electron density, as contrasted with the PFD procedure, where the total electron density $n_e(r)$ is used to define the DCF $C_{eI}(r)$.

In the second place, we show that the first equation determining $g_{II}(r)$ is quite sensitive to the error in $g_{eI}(r)$ contained in Eq. (16); in other words, the effective interionic potential $v^{eff}(r)$ to determine $g_{II}(r)$ is strongly dependent on $g_{eI}(r)$ specified by another coupled equation (14). The breakdown of the effective interionic potential given by Eq. (28) comes from $\rho_{DP}^{(1)}(Q)$ in Eq. (61), which contains the bound-electron contribution, as is shown in Fig. 1. Therefore, at this point let us replace $\rho_{DP}^{(1)}(Q)$ in Eq. (61) by $\rho_{DP}^{(0)}(Q)$; this replacement gives rise to the relation

$$S_{eI}(Q) = \frac{\rho_{DP}^{(0)}(Q)}{\sqrt{Z_I}} S_{II}(Q), \quad (65)$$

which is substituted in Eq. (4) to give an effective interionic potential in the form

$$\beta v^{eff}(Q) = \beta v_{II}^C(Q) + \beta v_{eI}^C(Q) \rho_{DP}^{(0)}(Q). \quad (66)$$

The approximation (65) to derive $v^{eff}(Q)$ of Eq. (66) is

equivalent to the replacement of $\beta v_{eI}^C(r)$ in $\Gamma_{eI}^{DP}(r)$ by $-C_{eI}^{DP}(r)$, while $\beta v_{eI}^C(r)$ in $\Gamma_{II}^{DP}(r)$ is retained as it is. Therefore, the breakdown shown previously is rescued by this improvement, since γ in Eq. (53) becomes zero in this approximation. The interionic potential $v^{eff}(r)$ calculated by Eq. (66) is plotted by the curve with solid circles in Fig. 3 along with the curve with crosses, which denotes $v^{eff}(r)$ calculated by Eq. (44) with the use of $C_{eI}^{DP}(Q)$ based on the jellium-vacancy model. In the same figure, the interionic potentials evaluated by the QHNC equation, by the QHNC equation with the step approximation for $g_{II}(r)$, and by the Ashcroft model potential are plotted by the solid curve, the curve with circles, and the dotted curve, respectively; the dashed curve is the result of Eq. (52). The procedure to determine the effective interionic potential by the QHNC equation is simplified by solving the DP equation with the step-function approximation, which is nothing else but the DRT procedure if the ion-ion RDF is approximated by the trapezoidal form instead of the step function. In the DRT method, the nonlocal pseudopotential with fitting parameters is determined so as to yield the nonlinear electron density in the linear response formula. In Fig. 4 the QHNC interionic potential at electron density $r_s = 3.25$ and plasma parameter $\Gamma = 200$ is compared with the DRT potential in conjunction with that obtained by the DP equation with the step-function approximation. The difference between the QHNC and DRT potentials near the potential minimum is ascribed to the trapezoidal approximation to $g_{II}(r)$ made in the DRT method, since there the DRT potential

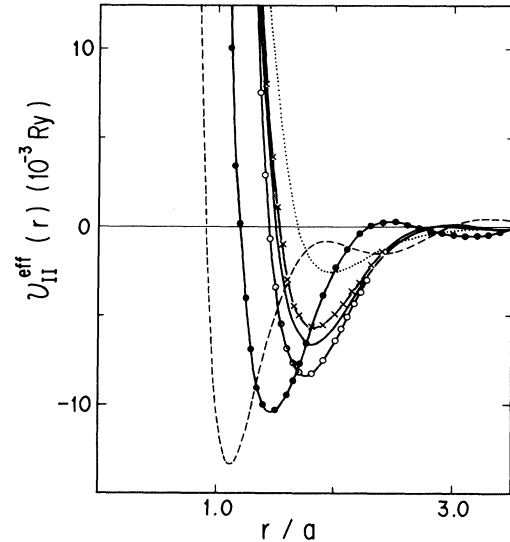


FIG. 3. Effective interionic potentials for a liquid lithium at 470 K with $r_s = 3.308$ and $\Gamma = 203.1$. The dashed curve, Eq. (52); the curve with solid circles, Eq. (66); the solid curve, the QHNC equation (44); the curves with white circles, the QHNC with the step-function approximation; the curve with crosses, the DP equation with the step-function approximation; and the dotted curve, the Ashcroft model potential.

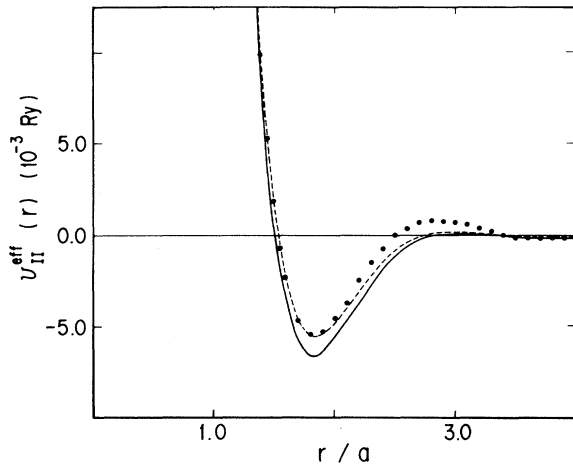


FIG. 4. Comparison between the QHNC and DRT interionic potentials at electron density $r_s = 3.25$. The solid and dotted curves indicate the potentials obtained by the QHNC equation and the DP equation with the step-function approximation, respectively, while the DRT potential is denoted by the solid circles.

shows good agreement with the DP potential. The deviation seen near $r/a = 2.8$ may come from the fitting procedure based on the nonlocal pseudopotential.

In Fig. 5 the ion-ion structure factors $S_{II}(Q)$ calculated by the above interatomic potentials are shown along with the experimental result [22] denoted by solid curve; the improved interatomic potential (66) does not give a good $S_{II}(Q)$ as is denoted by the dashed curve, while the interionic potential based on the nonlinear pseudopotential

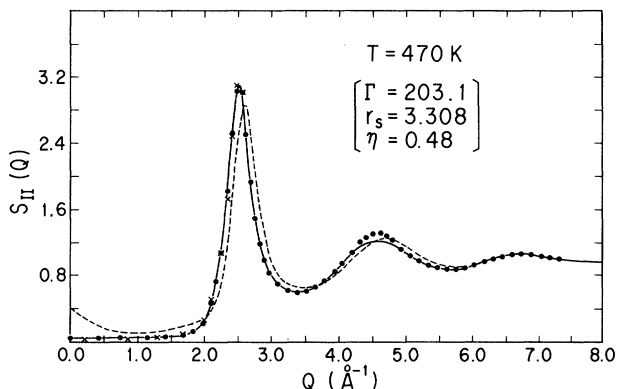


FIG. 5. Ion-ion structure factors for Li at 470 K; the solid circles denote the QHNC $S_{II}(Q)$ using parameters shown in this figure, while the solid curve is the experimental one. An improved interatomic potential given by Eq. (66) yields a structure factor significantly different from the experiment as shown by the dashed curve, while the potential based on $\rho_{DP}^{(0)}(r)$ of the jellium-vacancy model yields a good $S_{II}(Q)$ plotted by the crosses.

$-C_{el}^{DP}(Q)/\beta$ yields the structure factor plotted by the crosses, which show an excellent agreement with the solid circles, the QHNC result. Also, two other interatomic potentials shown in Fig. 3 except for the dashed curve of Eq. (52) provide the structure factors, which show no significant deviation from the QHNC result. This fact shows that the RDF $g_{II}(r)$ is not sensitive to the interionic potential as is well known; this is attributed to the fact that the RDF $g_{II}(r)$ is determined mainly by the repulsive part of the interionic potential and the bridge function. The improved interionic potential (66) is not accurate, as is shown by comparison of the structure factor based on Eq. (66) with the experimental one in Fig. 5, although the breakdown mentioned before does not occur in this approximation. Therefore, in order to give a more accurate description, we must also replace $\beta v_{el}^C(r)$ in $\Gamma_{II}^{DP}(r)$ with $-C_{el}^{DP}(r)/\beta$ as well as in $\Gamma_{el}^{DP}(r)$; these two replacements make the DP theory identical to the QHNC formulation.

In Fig. 6 the RDF's $g_{el}(r)$ obtained by various approximations are shown; the results based on the QHNC equation, the jellium-vacancy model, and the Ashcroft model potential are shown by the solid, dotted, and dashed curves, respectively. At this point, let us remember that the electron-ion structure factor can be evaluated by Eq. (65) with the use of the screening cloud $\rho_{DP}^{(0)}(Q)$ obtained by the jellium-vacancy model. The crosses in Fig. 6 indicate the RDF $g_{el}(r)$ calculated by the inverse Fourier transform of Eq. (65) combined with $\rho_{DP}^{(0)}(Q)$; the agreement with the QHNC result is quite good. It is interest-

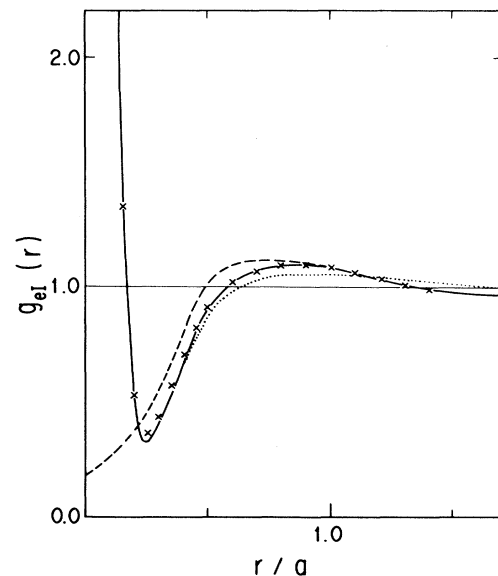


FIG. 6. The electron-ion radial distribution functions calculated by the QHNC equation, the DP method based on the jellium-vacancy model, and the linear response formula with the Ashcroft model potential are shown by the solid, dotted, and dashed curves, respectively. The crosses denote $g_{el}(r)$ obtained from Eq. (65) combined with $\rho_{DP}^{(0)}(r)$, which shows a fairly good agreement with the QHNC result.

ing to note that we can obtain more accurate $g_{el}(r)$ by this indirect procedure than by the direct calculation using the jellium-vacancy model, as may be seen from the comparison between the crosses and the dotted curve in Fig. 6.

IV. CONCLUDING DISCUSSION

The DP and QHNC formulations do not provide such great differences in treating a hydrogen plasma, when the bound-electron contribution is very small, that is, when $Z_I \approx Z_A$. However, it is shown that the DP theory breaks down when the bound-electron contribution becomes important in such a system, as exemplified by a liquid metal with $Z_B \gg 1$; its applicable limitation can be estimated roughly by the condition $\gamma < 1$, as described by Eq. (58). In spite of this fact, the second equation (14) can be used to determine a good nonlinear pseudopotential $w_b^{NL}(r)$ with the use of the step-function approximation (59) to the RDF $g_{II}(r)$ involved in Eq. (9); this equation turns out to be essentially identical with the treatment by DRT on the basis of the jellium-vacancy model. It is important to realize that the nonlinear pseudopotential $-C_{el}^{DP}(r)/\beta$ is defined in terms of the free-electron density $n_e^f(r) = n_0^e g_{el}(r)$ only. This contrasts with the PFD treatment [20], where the bound-electron density $n_e^b(r)$ is involved in the definition of the non-Coulomb part of the DCF $C_{el}(Q)$ in the form

$$C_{el}^{NC, PFD}(Q) \equiv C_{el}^{PFD}(Q) - \beta \frac{3\pi Z_A}{Q^2} \equiv \frac{S_{el}(Q) + n_e^b(Q)/\sqrt{Z_I}}{\sqrt{n_0^I n_0^e} \chi_Q^0} + \beta V_e(Q), \quad (67)$$

while Eq. (14) is written by the Fourier transform

$$C_{el}^{NC, DP}(Q) \equiv C_{el}^{DP}(Q) - \beta \frac{4\pi Z_I}{Q^2} \equiv \frac{S_{el}(Q)}{\sqrt{n_0^I n_0^e} \chi_Q^0} + \beta V_e(Q). \quad (68)$$

Therefore, the long-range behavior is different between $C_{el}^{PFD}(r)$ and $C_{el}^{DP}(r)$, since Eq. (67) contains the nuclear charge Z_A in contrast with the ionic charge Z_I in Eq. (68). The second different point compared with the PFD treatment exists in the expression for the total exchange-correlation potential $W_e^{ee}(r)$, which is approximated in Eq. (12), in the form

$$W_e^{ee}(r) = \mu_{XC}(n_e^b(r) + n_0^e) - \mu_{XC}(n_0^e) + \int \frac{C_{ee}^{XC, DP}(|\mathbf{r} - \mathbf{r}'|)}{-\beta} \delta n_e^f(r') d\mathbf{r}', \quad (69)$$

while the PFD approach uses an approximate expression,

$$W_e^{ee}(r) = \int \frac{C_{ee}^{XC, PFD}(|\mathbf{r} - \mathbf{r}'|)}{-\beta} [\delta n_e^f(r') + n_e^b(r')] d\mathbf{r}'. \quad (70)$$

It is to be noted at this point that the exchange-correlation potential $W_e^{ee}(r)$ caused by the electrons in

the system must be divided into the bound-electron and free-electron contributions, as is described by Eq. (69), since the free-electron part of the exchange-correlation potential $C_{ee}^{XC, DP}(Q)$ leads to the density response function

$$\chi_Q^0 / [1 - n_0^e C_{ee}^{DP}(Q) \chi_Q^0] = \chi_Q^{jell},$$

in such a form as Eqs. (62) and (44). Therefore, it is appropriate to treat the free-electron part of the exchange-correlation potential in the nonlocal form using the LFC $G(Q)$ as described by Eq. (47); the exchange-correlation factor defined by Eq. (11) should not contain the bound-electron contribution. Due to these two different approximations given by Eqs. (67) and (70), the PFD approach is not appropriate to treat a system with a significant bound-electron contribution, although their equations takes account of the electron-ion correlation by using the QHNC approximation. It is worth noting that the bound-electron density $n_e^b(r)$ should be absorbed in the electron-ion potential (7) and the bare ion-ion interactions (6). There is no clear concept of an "ion" in the PFD scheme, as shown by the example that a bare ion-ion interaction in the PFD scheme is defined by $v_{II}^{PFD}(r) = Z_A Z_I / r$ and, as a consequence, their DCF $C_{II}^{PFD}(r)$ in the long-range approaches $-\beta Z_A Z_I / r$ in contrast with $C_{II}^{DP}(r) \approx -\beta Z_I^2 / r$, which results from Eq. (13).

The breakdown of the DP theory comes from the second equation (14), which cannot yield a sufficiently accurate RDF $g_{el}(r)$ to be inserted in Eq. (16) determining the RDF $g_{II}(r)$ based on the first equation (13), although the second equation (14) can provide an excellent nonlinear pseudopotential $w_b^{NL}(r) = -C_{el}(r)/\beta$. Nevertheless, this comparison between the DP theory and the QHNC equation suggests the following simple scheme to calculate the correlations in strongly coupled plasmas:

(i) In the first step, we obtain the nonlinear pseudopotential $w_b^{NL}(r) = -C_{el}(r)/\beta$ by solving the second equation (14) with the use of the step-function approximation for $g_{II}(r)$ (the jellium-vacancy model), as was mentioned in Sec. III. Here, the electron density n_0^e must be determined to be consistent with Z_B of an "ion" fixed at the center of the vacancy in the jellium in such a way as to be $n_0^e = (Z_A - Z_B) n_0^I$ with $Z_B = \int n_e^b(r) d\mathbf{r}$.

(ii) In the second step, the effective interionic potential $v^{eff}(r)$ can be constructed by Eq. (44) with use of $w_b^{NL}(Q)$ in the first step, and then the modified HNC equation for this interionic potential is solved to obtain $g_{II}(r)$, which yields the structure factor $S_{II}(Q)$.

(iii) In the last, the electron-ion structure factor $S_{eI}(Q)$ can be evaluated by Eq. (65) or Eq. (32). In this way, we can obtain the ionic charge Z_I , the electron cloud $\rho(r)$ of a pseudoatom, the pseudopotential $w_n^{NL}(r)$, the interionic potential $v^{eff}(r)$, and the RDF's $g_{II}(r)$ and $g_{el}(r)$ in a plasma. The quantities calculated by this procedure are shown to coincide excellently with the QHNC results in Figs. 1–6 for the case of a liquid Li. However, note that this approach can be applied only to the system which has a small isothermal compressibility κ , since we have used the relation

$$n_0^I \mathcal{F}_{Q=0}[\Theta(r - R_{ws}) - 1] = 0 \approx S_{II}(0)$$

in the jellium-vacancy model. In order to obtain a more refined result for a strongly coupled plasma, these quantities based on the jellium-vacancy model can be used as initial-guess data in solving the QHNC equation [9] for a nucleus-electron mixture, as was done in the case of a liquid lithium [10].

In conclusion, the QHNC equation is shown to be applicable to systems with the large bound-electron contribution exemplified by a liquid metallic lithium, whereas the DP theory breaks down due to the neglect of the electron-ion correlation. It is well known that in a simple liquid metal a bare electron-ion interaction is considered to be weak owing to the presence of bound electrons around a nucleus, as is represented by a pseudopotential $w_b(r)$. The electron-ion correlation neglected in the DP theory is the non-Coulomb part of the electron-ion DCF, $C_{el}^{NC}(r)$, which reduces the strength of a bare electron-ion interaction $v_{el}^C(r)$ in the DP equation by replacing it with a pseudopotential

$$w_b^{NL}(r) = v_{el}^C(r) - C_{el}^{NC}(r)/\beta = -C_{el}(r)/\beta$$

so “weak” that it provides an *exact* screening cloud $\rho(r)$ in the *linear* response formula (33). This is the reason the DP theory cannot deal with “ions,” when the bound-electron contribution becomes important. Although the PFD approach takes account of the electron-ion correlation in the QHNC approximation, it does not work well in a liquid metal, since in their scheme the bound-electron density $n_e^b(r)$ is not appropriately treated. However, it should be mentioned that the applicability of the QHNC approach described in Eqs. (30)–(45) is limited to “simple metallic” systems, where the core-electron overlap is small and there is no significant resonant state, since the bare ion-ion interaction in Eq. (44) is taken as the pure Coulomb potential $v_{II}^C(r)$ and the ionic charge Z_I is defined simply in terms of the electron number Z_B belonging to the bound states. In order to treat a “non-simple metallic” system, the QHNC equation must be improved to take account of the overlap of core electrons and the resonance states; such an improvement is planned to be reported elsewhere.

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