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Structure factor and pseudopotential of liquid metallic lithium determined from the nucleus-electron model

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By treating a liquid metal as a mixture consisting of nuclei and electrons, we have derived a set of integral equations for calculating radial distribution functions (RDF's) from the atomic number as the only input data; the internal atomic structure of an ion in a liquid metal is obtained self-consistently with the liquid structure at the same time. Here, we apply this formulation to liquid metallic lithium using further two approximations: (1) the local-field correction factor for electrons in a liquid metal is approximated by that of the jellium model, and (2) the ion-ion bridge function is replaced by that of the Percus-Yevick equation for a hard-sphere fluid. We calculate the structure factors at 470 and 595 K, which show excellent agreement with the experimental ones. Simultaneously we obtain the electron-ion RDF, which gives the charge distribution $\rho(r)$ of a neutral pseudoatom taking account of nonlinear screening. We extract a nonlinear pseudopotential $w_b^{\mathrm{nl}}(r)$ from the density $\rho(r)$; this yields an interatomic interaction $v^{\mathrm{eff}}(r)$ giving the ion-ion RDF. Thus we determine the ion-ion and electron-ion RDF's, the charge distribution $\rho(r)$ of a pseudoatom, the pseudopotential $w_b^{\mathrm{nl}}(r)$, and the pair interaction $v^{\mathrm{eff}}(r)$ in a self-consistent manner; they are also regarded as consistent with experiment.

I. INTRODUCTION

In the standard procedure[1] to determine the structure of a metallic liquid, the problem is solved by the following two steps: (1) the construction of a pseudopotential which provides an effective interatomic pair interaction, and (2) the evaluation of the liquid structure with the use of the pair interaction obtained in the first step using a method of liquid theory, such as integral equations. In reality a liquid metal is a coupled ion-electron mixture; nevertheless, the presence of the electrons is taken into account only in the determination of a pair interaction in this approach, and after that a liquid metal is viewed as a quasi-one-component system consisting of ions only. Since an effective pair interaction is constructed by applying the linear-response formula using a pseudopotential, this approach is evidently valid only for the system whose electron-ion interaction is sufficiently weak. Moreover, it happens to become necssary for some liquid metals which have a strong electron-ion correlation that many-body forces such as a three-body interaction be introduced to describe the system in addition to a two-body one, since the two steps as mentioned above are quite independent of each other.

In contrast to this situation, in the usual treatment of a liquid metal, the electronic structure of atoms and solids, for example, can be calculated on the basis of density-functional theory,[2-5] only if the atomic number of the system is known as the input data, at the present stage. In a similar way, the structure of a liquid metal may be determined from knowledge of the atomic number Z_A as the only input data, when we treat a liquid metal as a nucleus-electron mixture instead of modeling as an "ion"-electron mixture, since the interparticle interactions are all Coulombic in this model. However, it may be more difficult in some sense to determine the electronic and liquid structure of a liquid metal with this model than to obtain the band structure of a solid; the reason for this is that the positions of the nuclei are given beforehand in the case of a band calculation, while in a liquid metal the configuration of ions must be determined self-consistently with the electronic structure of valence and bound electrons in the system. If this approach is possible, there occurs no condition in dealing with a liquid metal that an electron-ion interaction should be weak, as is required in the pseudopotential theory based on the linear-response formula. Moreover, a liquid metal can always be described only by an effective pairwise interaction with the density-functional theory based on the nucleus-electron model, since this scheme reduces the many-body problem to the one-body problem under an effective external potential.

Previously, by applying the density-functional formalism to the nucleus-electron mixture we have derived a set of integral equations for correlations in a liquid metal as an ion-electron mixture in conjunction with the condition that the ionic structure and the electron-ion interaction are determined self-consistently with the liquid structure.[6] Already we have calculated the ion-ion and electron-ion radial distributions (RDF's) for a liquid metallic hydrogen[7] or a fully ionized hydrogen plasma[8] using the quantal hypernetted-chain (QHNC) equation[9] set-up for an ion-electron mixture; this system is the simplest one in the sense that there is no ionic structure and the electron-ion interaction is pure Coulombic. It is of interest to apply our method to a liquid metal with ionic core electrons and to know to what extent the calculation can give the structure factor, in agreement with experiment, using the atomic number as the only input data. Moreover, in a plasma such as that produced by laser compression, for example, the ionic valency Z_I and the electron-ion interaction $v_{e\text{-}I}(r)$ may vary over a wide range as its temperature and density change. As a consequence, it is significant in the treatment of plasmas that our method based on the nucleus-electron model can calculate these quantities in a self-consistent manner from the atomic number of the system. A liquid metal can be considered as one kind of a high-density plasma. Therefore, before applying this formulation to a plasma, the experiments of which are difficult to perform with sufficient precision, it is important to apply it to liquid metals which have a great deal of reliable experimental information, and to ascertain the validity of the theory by comparing with experiment. As the first application of our theory to a liquid metal with core electrons, we choose lithium, since it has the fewest bound electrons forming ions in liquid metals: the two 1*s* electrons in a liquid state.

In Sec. II, we sketch the derivation of integral equations for correlations in a liquid metal using the nucleus-electron model,[6] which has proved to lead to the ion-electron model described in the first part of Sec. II. Also, some important comments on treating a liquid metal are added from the viewpoint of our formulation. Next, we solve these integral equations applied to a liquid metallic lithium, and compare the result with experiment in Sec. III. The general comments given in Sec. II are exemplified there in the case of liquid metallic lithium. Section IV is devoted to a concluding discussion.

II. SUMMARY OF FORMULATION

In this section we give an outline of treatment of a liquid metal, first on the basis of the ion-electron model and second on the nucleus-electron model. For details, see Refs. 7 and 6. In the first approach, a liquid metal is considered as a mixture of ions and electrons; the former can be treated as classical particles and the latter behaves as a quantum fluid. Because ions are classical particles, the electron-ion and ion-ion RDF's are equal to the electron and ion density distributions around a fixed ion in a liquid metal, respectively. Since a fixed ion causes external potentials $U_i(r) \equiv v_{i\text{-}I}(r)$ [with interparticle interactions $v_{ij}(r)$] acting on ions ($i = I$) and electrons ($i = e$), the problem of determining the RDF's is altered to evaluate the inhomogeneous density distributions under external potentials applied to a homogeneous liquid metal. Therefore, on the basis of the density-functional theory[2-5] we can obtain exact expressions for the ion-ion and electron-ion RDF's, $g_{I\text{-}I}(r)$ and $g_{e\text{-}I}(r)$, in terms of the density distributions of noninteracting systems $n_i^0(r\,|\,U_i^{\text{eff}})$ under effective external potentials $U_i^{\text{eff}}(r)$:

$$g_{I\text{-}I}(r) = n_I(r/I)/n_0^I = n_I^0(r|v_{I\text{-}I}^{\text{eff}})/n_0^I \ , \tag{1}$$

$$g_{e\text{-}I}(r) = n_e(r|I)/n_0^e = n_e^0(r|v_{e\text{-}I}^{\text{eff}})/n_0^e \ , \tag{2}$$

where

$$n_I^0(r|U) \equiv n_0^I \exp[-\beta U(r)] \ , \tag{3}$$

for ions being classical particles, and

$$n_e^0(r|U) \equiv \sum_l f(\epsilon_l)|\phi_l(r)|^2 \ , \tag{4}$$

for electrons constituting a quantum fluid, with

$$f(\epsilon) \equiv \{\exp[\beta(\epsilon - \mu_e^0)] + 1\}^{-1} \ . \tag{5}$$

In the above the electron density, $n_e^0(r|U)$ is calculated by solving the wave equation for an electron under the external potential $U(r)$:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(r) \right] \phi_l(r) = \epsilon_l \phi_l(r) \ . \tag{6}$$

Here, the effective external interactions $U_i^{\text{eff}}(r) \equiv v_{i\text{-}I}^{\text{eff}}(r)$ are given by

$$v_{i\text{-}I}^{\text{eff}}(r) = v_{i\text{-}I}(r) + \frac{\delta \mathcal{F}_{\text{int}}}{\delta n_i(\mathbf{r}|I)} - \mu_i^{\text{int}} \ , \tag{7}$$

with the use of $\mathcal{F}_{\text{int}}$ and μ_i^{int}, the interaction part of the intrinsic free energy and the chemical potentials of the system, respectively. These effective interactions can be rewritten by expanding with respect to the density deviations from the uniform densities n_0^i in the forms

$$\begin{aligned} v_{ij}^{\text{eff}}(r) &= v_{ij}(r) + \sum_l \int \left. \frac{\delta^2 \mathcal{F}_{\text{int}}}{\delta n_i(\mathbf{r})\delta n_l(\mathbf{r}')} \right|_0 \\ &\quad \times \delta n_l(\mathbf{r}'|j) d\mathbf{r}' - B_{ij}(r)/\beta \\ &= v_{ij}(r) - \Gamma_{ij}(r)/\beta - B_{ij}(r)/\beta \ , \end{aligned} \tag{8}$$

with

$$\Gamma_{ij}(r) \equiv \sum_l \int C_{il}(|\mathbf{r}-\mathbf{r}'|)[n_l(r'|j) - n_0^l] d\mathbf{r}' \ , \tag{9}$$

on using the bridge functions $B_{ij}(r)$ and the direct correlation functions[5] (DCF) defined by

$$C_{ij}(|\mathbf{r}-\mathbf{r}'|) \equiv -\beta \left. \frac{\delta^2 \mathcal{F}_{\text{int}}}{\delta n_i(\mathbf{r})\delta n_j(\mathbf{r}')} \right|_{U=0} \ . \tag{10}$$

At this point, it should be noted that the ion-ion RDF $g_{I\text{-}I}(r)$ in the two-component system can be taken as the RDF of a one-component fluid interacting via an effective interaction:[7(b)]

$$\beta v^{\text{eff}}(Q) = \beta v_{I\text{-}I}(Q) - |C_{e\text{-}I}(Q)|^2 \frac{n_0^e \chi_Q^0}{1 - n_0^e C_{e\text{-}e}(Q)\chi_Q^0} \ , \tag{11}$$

since $v_{I\text{-}I}^{\text{eff}}(r)$ can be rewritten as

$$\begin{aligned} \beta v_{I\text{-}I}^{\text{eff}}(r) = \beta v^{\text{eff}}(r) - n_0^I \int C(|\mathbf{r}-\mathbf{r}'|)[g_{I\text{-}I}(r') - 1] \\ \times d\mathbf{r}' - B_{I\text{-}I}(r) \ , \end{aligned} \tag{12}$$

with the help of the definition of the one-component DCF,

$$n_0^I C(Q) = 1 - 1/S_{I\text{-}I}(Q) \ , \tag{13}$$

in terms of the ion-ion structure factor in a liquid metal. In the density-functional scheme, where the RDF's can be exactly defined as the density distributions under some effective external potentials, it is important to notice that a pair-potential description of a liquid metal as a one-component system is always possible on the basis of Eq. (11) and we need not introduce many-body forces, provided that a liquid metal can be taken as an ion-electron mixture. If we use the effective interparticle interaction (11) for a liquid metal, the bridge function of this one-component system should become identical with $B_{I\text{-}I}(r)$, that of the two-component system as an ion-electron mixture.

The Fourier transforms of the DCF's (10) can be expressed in the matrix form

$$\sqrt{\mathcal{N}}C(Q)\sqrt{\mathcal{N}}=(\chi_Q^0)^{-1}-(\chi_Q)^{-1}\ , \tag{14}$$

using the density response functions $\chi_Q\equiv\|\chi_Q^{ij}\|$ and $\chi_Q^0\equiv\|\chi_Q^{0i}\delta_{ij}\|$ of the interacting and noninteracting systems, respectively, and $\mathcal{N}\equiv\|n_0^i\delta_{ij}\|$. Therefore, the expressions for the partial structure factors $S_{I\text{-}I}(Q)$ and $S_{e\text{-}I}(Q)$ are obtained inversely from (14) in terms of the DCF's $C_{ij}(Q)$ and the density response function $\chi_Q^0\equiv\chi_Q^{0e}$ of the noninteracting system in the forms

$$S_{I\text{-}I}(Q)=[1-n_0^I C_{e\text{-}e}(Q)\chi_Q^0]/D(Q)\ , \tag{15}$$

$$\begin{aligned}S_{e\text{-}I}(Q)&=(n_0^e n_0^I)^{1/2}C_{e\text{-}I}(Q)\chi_Q^0/D(Q)\\&=\frac{\rho(Q)}{\sqrt{Z_I}}S_{I\text{-}I}(Q)\ ,\end{aligned} \tag{16}$$

with

$$\rho(Q)\equiv n_0^e C_{e\text{-}I}(Q)\chi_Q^0/[1-n_0^e C_{e\text{-}e}(Q)\chi_Q^0]\ , \tag{17}$$

$$\begin{aligned}D(Q)=&[1-n_0^I C_{I\text{-}I}(Q)][1-n_0^e C_{e\text{-}e}(Q)\chi_Q^0]\\&-n_0^3 n_0^I|C_{e\text{-}I}(Q)|^2\chi_Q^0\ .\end{aligned} \tag{18}$$

Here, we have used the fact that the density response functions $\chi_Q^{i\text{-}I}$ concerning ions ($i=I$ or $i=e$) become identical with the structure factors $S_{i\text{-}I}(Q)$ and $\chi_Q^{0I}=1$, since the ions in a liquid metal can be treated as classical particles. In particular, Eq. (16) can be represented in the r space as

$$n_0^e g_{e\text{-}I}(r)=\rho(r)+n_0^I\int\rho(|\mathbf{r}-\mathbf{r}'|)g_{I\text{-}I}(r')d\mathbf{r}'\ , \tag{19}$$

which states that the valence-electron distribution around an ion can be expressed exactly by the superposition of surrounding "neutral pseudoatoms;"[10] each ion carries about a screening electron cloud $\rho(r)$, which has a charge $\int\rho(r)d\mathbf{r}=Z_I$ and therefore makes it electrically neutral as if it were an atom. In this respect, it should be emphasized that any liquid metal (or plasma) can always be regarded as composed of neutral pseudoatoms irrespective of the strength of ion-electron interaction, as shown by Eq. (19), which is derived without use of any approximation. In the usual theory of liquid metals, using the jellium model, the screening cloud $\rho(r)$ is determined by the linear-response formula for the induced density in an electron gas by a fixed ion with a pseudopotential $w_b(r)$ as follows:

$$\begin{aligned}\rho(Q)&\simeq-n_0^e\beta w_b(Q)\chi_Q^0/[1-n_0^e C_{e\text{-}e}^{\text{jel}}(Q)\chi_Q^0]\\&=-n_0^e\beta w_b(Q)\chi_Q^{\text{jel}}\ .\end{aligned} \tag{20}$$

This is also obtained from Eq. (17) in the following approximations:

$$C_{e\text{-}I}(Q)\simeq-\beta w_b(Q)\ , \tag{21}$$

$$C_{e\text{-}e}(Q)\simeq C_{e\text{-}e}^{\text{jel}}(Q)\ , \tag{22}$$

which means that the DCF of two-component system $C_{e\text{-}e}(Q)$ is approximated by that of the jellium model $C_{e\text{-}e}^{\text{jel}}(Q)$; thus Eq. (17) becomes a linear-response expression for $\rho(r)$ with the response function of the jellium model χ_Q^{jel}. Since a screening electron cloud $\rho(r)$ is exactly represented in terms of $C_{e\text{-}I}(Q)$ by Eq. (17), we can think of the DCF $C_{e\text{-}I}(r)$ as playing the role of a pseudopotential $w_b^{\text{nl}}(r)$, which can take into account nonlinear screening in the same form as that of the linear-response formula (20).

When we treat a liquid metal as a mixture of ions and electrons, the ion charge Z_I and the electron-ion interaction $v_{e\text{-}I}(r)$ must be given beforehand. These quantities can be determined from the first principles, if a liquid metal is taken more fundamentally as a mixture of nuclei and electrons.[6] Then interparticle interactions are only Coulombic, and the only input data necessary are the atomic number Z_A of the system, in order to determine the structure of a liquid metal and the internal electronic structure of an ion in a liquid state. Here, let us treat a liquid metal as a mixture consisting of N_I nuclei and Z_AN_I electrons. We single out one nucleus and fix it at the origin. Then a fixed nucleus causes an external potential $v_{e\text{-}N}(r)=-Z_Ae^2/r$ acting on the system consisting of other (N_I-1) nuclei and Z_AN_I electrons. It should be remembered here that the density-functional formalism contains some arbitrariness of the choice of a reference system to describe this inhomogeneous system.[5] Therefore, in order to obtain a simpler description of the inhomogeneous nucleus-electron mixture, we take as a reference system a mixture consisting of (N_I-1) noninteracting ions and $Z_I(N_I-1)+Z_A$ noninteracting electrons; each ion is assumed to have Z_B bound electrons with a distribution $\rho_b(r)$ around it and an ionic charge $Z_I\equiv Z_A-Z_B$. The values of Z_B and $\rho_b(r)$ are to be determined self-consistently. Hereafter, this reference system will be referred to as the average ion model. The density-functional formalism gives an effective external potential for electrons around the fixed nucleus:

$$v_{e\text{-}N}^{\text{eff}}(r)=v_{e\text{-}N}(r)+\frac{\delta\mathcal{F}_{\text{int}}}{\delta n_e(\mathbf{r})}-\mu_e^{\text{int}}\ , \tag{23}$$

in terms of $\mathcal{F}_{\text{int}}=\mathcal{F}-\mathcal{F}_0$, the difference of intrinsic free energy between the real and reference systems $\mathcal{F}$ and $\mathcal{F}_0$, respectively. Thus, the electron distribution $n_e(r|N)$ around the fixed nucleus is determined by solving the wave equation (6) with respect to the effective potential (23) as follows:

$$n_e(r|N)=n_e^0(r|v_{e\text{-}N}^{\text{eff}})\equiv n_e^b(r|N)+n_e^v(r|N)\ . \tag{24}$$

Here, n_e^b and n_e^v denote the bound- and valence-electron distributions, respectively. When we position ourselves at the nucleus fixed at the origin, we can see a world, where some bound electrons move around it, the valence electrons are accumulated, as described in Eq. (24), and other ions are pushed away from it. On the other hand, even if we position ourselves at any nucleus in the reference system, we must see the same world viewed from the nucleus fixed at the origin. Therefore, the bound-electron distribution $\rho_b(r)$ of the average ion in the reference system should be identical to the bound-electron distribution $n_b(r|N)$ around the central fixed nucleus, i.e.,

$$\rho_b(r)=n_e^b(r|N) \ . \tag{25}$$

As a result, the bound-electron number Z_B of the average ion is given by

$$Z_B\equiv\int\rho_b(r)d\mathbf{r}=\sum_{l\in\text{bound}}\frac{1}{\exp[\beta(\epsilon_l-\mu_e^0)]+1} \ , \tag{26}$$

where the ϵ_l's are electron bound levels of the central fixed nucleus. As a consequence, the charge neutrality condition $n_0^e=Z_I n_0^I$ leads to the equation to determine the chemical potential μ_e^0 of electrons:

$$Z_A=\frac{1}{n_0^I}\int\frac{2}{\exp[\beta(p^2/2m-\mu_e^0)]+1}\frac{1}{(2\pi)^3}d\mathbf{p}$$
$$+\sum_{l\in\text{bound}}\frac{1}{\exp[\beta(\epsilon_l-\mu_e^0)]+1} \ , \tag{27}$$

because of the relation

$$\lim_{r\to\infty}n_e(r|N)=\frac{1}{V}\sum_{i\in\text{valence}}\frac{1}{\exp[\beta(\epsilon_i-\mu_e^0)]+1}$$
$$=n_0^e \ . \tag{28}$$

In this way, the average ion structure in the premise at the beginning can be determined self-consistently by Eqs. (23)–(27).

In order to obtain a tractable expression for $v_{e\text{-}N}^{\text{eff}}(r)$, we introduce here two approximations to the chemical potential involved in (23),

$$\frac{\delta\mathcal{F}_{\text{int}}}{\delta n_e(\mathbf{r})}\equiv\mu_{e\text{-}I}(r|n_I n_e)+\mu_{e\text{-}e}^{\text{xc}}(r|n_I n_e)$$
$$+\int v_{e\text{-}e}(|\mathbf{r}-\mathbf{r}'|)n_e(r')d\mathbf{r}' \ . \tag{29}$$

(i) The electron-ion interaction part of the chemical potential $\mu_{e\text{-}I}(r|n_I n_e)$ is approximated by the functional expansion with respect to the density deviation up to the first order, i.e., the hypernetted-chain (HNC) approximation,

$$\mu_{e\text{-}I}(r|n_I n_e)\simeq\int\frac{C_{e\text{-}I}(|\mathbf{r}-\mathbf{r}'|)}{-\beta}\delta n_I(r')d\mathbf{r}'. \tag{30}$$

(ii) The exchange-correlation potential $\mu_{e\text{-}e}^{\text{xc}}(r|n_I n_e)$ for electrons in a liquid metal is represented by the local-density approximation to the bound electrons and by the HNC approximation to the valence electrons:

$$\mu_{e\text{-}e}^{\text{xc}}(r|n_I n_e)\simeq\mu_{\text{xc}}(n_e^b(r|N)+n_0^e)-\mu_{\text{xc}}(n_0^e)$$
$$+\int\frac{C_{e\text{-}e}^{\text{xc}}(|\mathbf{r}-\mathbf{r}'|)}{-\beta}\delta n_e^v(r')d\mathbf{r} \ . \tag{31}$$

Here, $C_{e\text{-}e}^{\text{xc}}(r)\equiv C_{e\text{-}e}(r)+\beta v_{e\text{-}e}(r)$. From Eq. (23), with these approximations, the effective potential for electrons around the fixed nucleus based on the electron-nucleus model is shown to become identical with the effective electron-ion potential in an electron-ion mixture represented in the form

$$v_{e\text{-}I}^{\text{eff}}(r)=\tilde{v}_{e\text{-}I}(r)+\int\frac{C_{e\text{-}e}(|\mathbf{r}-\mathbf{r}'|)}{-\beta}\delta n_e^v(r')d\mathbf{r}'$$
$$+\int\frac{C_{e\text{-}I}(|\mathbf{r}-\mathbf{r}'|)}{-\beta}[n_I(r'|I)-n_0^I]d\mathbf{r}' \ . \tag{32}$$

This is essentially equal to $v_{e\text{-}I}^{\text{eff}}(r)$ given by Eq. (8), except that the bare electron-ion interaction is now given in a self-consistent manner in the form

$$\tilde{v}_{e\text{-}I}(r)\equiv v_{e\text{-}N}(r)+\int v_{e\text{-}e}(|\mathbf{r}-\mathbf{r}'|)n_e^b(r'|N)d\mathbf{r}'$$
$$+\mu_{\text{xc}}(n_e^b(r|N)+n_0^e)-\mu_{\text{xc}}(n_0^e) \ . \tag{33}$$

Thus we find that the treatment of a liquid metal as a nucleus-electron mixture in the average ion model is shown to lead to the ion-electron mixture model,[8] where the electron-ion interaction $\tilde{v}_{e\text{-}I}(r)$ and the atomic structure of the ion $\rho_b(r)$ can be determined in a self-consistent way.

Concerning the effective electron-ion interaction (32), it is interesting to note that the following three types of approximate expressions for $v_{e\text{-}I}^{\text{eff}}$ can be derived from it, when we apply the random-phase approximation (RPA) to Eq. (32):

$$C_{e\text{-}I}(r)\simeq-\beta\tilde{v}_{e\text{-}I}(r) \ . \tag{34}$$

The first one is written as

$$v_{e\text{-}I}^{\text{eff}}(r)\simeq\tilde{v}_{e\text{-}I}(r)+n_0^I\int\tilde{v}_{e\text{-}I}(|\mathbf{r}-\mathbf{r}'|)[g_{I\text{-}I}(r')-1]d\mathbf{r}'$$
$$+\int\frac{C_{e\text{-}e}(|\mathbf{r}-\mathbf{r}'|)}{-\beta}\delta n_e^v(r')d\mathbf{r}' \ , \tag{35}$$

which shows that because of $\tilde{v}_{e\text{-}I}(r)\simeq Z_I e^2/r$ the effective potential for electrons around a nucleus can be approximated as a superposition of the ions surrounding it, in addition to the contribution of valence electrons. This expression can be rewritten approximately in the second form

$$v_{e\text{-}I}^{\text{eff}}(r)\simeq v_{\text{pa}}(r)+n_0^I\int v_{\text{pa}}(|\mathbf{r}-\mathbf{r}'|)[g_{I\text{-}I}(r')-1]d\mathbf{r}' \ , \tag{36}$$

with

$$v_{\text{pa}}(r)\equiv v_{e\text{-}N}(r)+n_0^I\int v_{e\text{-}e}(|\mathbf{r}-\mathbf{r}'|)\rho_{\text{pa}}(r')d\mathbf{r}'$$
$$+\mu_{\text{xc}}(\rho_{\text{pa}}(r)) \ , \tag{37}$$

$$\rho_{\text{pa}}(r)\equiv\rho_b(r)+\rho(r) \ , \tag{38}$$

which is derived by the aid of Eq. (19). Since $\rho_{\text{pa}}(r)$ denotes the electron density distribution of the neutral pseudoatom including bound electrons, Eq. (36) shows that the effective potential for electrons produced by the nucleus at the origin can be constructed by the superposition of neutral pseudoatoms around it. This relation gives a foundation to the Mattheiss procedure[11] to construct the muffin-tin potential in the calculation of the band structure by the superposition of potentials caused by free neutral atoms, since the density distribution of the neutral pseudoatom is almost the same as that of a free atom, as will be shown later numerically. Finally, the third type of approximate expression for $v_{e\text{-}I}^{\text{eff}}(r)$ is obtained by replacing $\tilde{v}_{e\text{-}I}(r)$ in Eq. (32) with $-C_{e\text{-}I}(r)/\beta$ as follows:

$$v_{e\text{-}I}^{\mathrm{eff}}(r) \simeq w(r) + n_0^I \int w(|\mathbf{r}-\mathbf{r}'|)[g_{I\text{-}I}(r')-1]d\mathbf{r}' \ , \tag{39}$$

where

$$\mathcal{F}_Q[w(r)] = \frac{-C_{e\text{-}I}(Q)/\beta}{1-n_0^e C_{e\text{-}e}(Q)\chi_Q^{0e}} \ . \tag{40}$$

This is essentially the same as the muffin-tin potential given by Meyer and Young.[12] Here, note that Eq. (39) can be applied only as a potential for valence electrons in a liquid metal.

Now, on the basis of the nucleus-electron model, the integral equations for the structure of a liquid metal are written in the alternative forms for the DCF's

$$C_{I\text{-}I}(r) = \exp[-\beta v_{I\text{-}I}(r) + \Gamma_{I\text{-}I}(r) + B_{I\text{-}I}(r)] - 1 - \Gamma_{I\text{-}I}(r) \ , \tag{41}$$

$$C_{e\text{-}I}(r) = \hat{B}^{\,-1}[n_e^{0v}(r|\tilde{v}_{e\text{-}I} - \Gamma_{e\text{-}I}/\beta - B_{e\text{-}I}/\beta)/n_0^e - 1] - \Gamma_{e\text{-}I}(r) \ . \tag{42}$$

These are the rewritten forms of (1) and (2) by the use of the Ornstein-Zernike (OZ) relations for the mixture

$$g_{I\text{-}I}(r) - 1 = C_{I\text{-}I}(r) + \Gamma_{I\text{-}I}(r), \tag{43}$$

$$g_{e\text{-}I}(r) - 1 = \hat{B}C_{e\text{-}I}(r) + \hat{B}\Gamma_{e\text{-}I}(r) \ , \tag{44}$$

where $\hat{B}$ denotes an operator defined by

$$\mathcal{F}_Q[\hat{B}^{\,\alpha} f(r)] \equiv (\chi_Q^0)^\alpha \mathcal{F}_Q[f(r)] = (\chi_Q^0)^\alpha \int e^{i\mathbf{Q}\cdot\mathbf{r}} f(r) d\mathbf{r} \ , \tag{45}$$

for an arbitrary real number α. Here, it should be noted that only the valence-electron part of density distribution $n_e^{0v}(r|v_{e\text{-}I}^{\mathrm{eff}})$ is taken in Eq. (42) to evaluate the electron-ion RDF $g_{e\text{-}I}(r) \equiv n_e^{0v}(r|v_{e\text{-}I}^{\mathrm{eff}})/n_0^e$, and that the bound-electron part $n_e^b(r|N)$ is only involved in the electron-ion interaction $\tilde{v}_{e\text{-}I}(r)$ defined by Eq. (33) to provide the screening and exchange-correlation effects due to bound electrons.

III. APPLICATION TO LIQUID METALLIC LITHIUM

In order to obtain the closed integral equations for the DCF's $C_{I\text{-}I}(r)$ and $C_{e\text{-}I}(r)$ we must introduce further two approximations to $C_{e\text{-}e}(r)$ and $B_{I\text{-}I}(r)$, which are contained in Eqs. (41) and (42) as unknown functions, in addition to the HNC approximation $B_{e\text{-}I}(r)=0$ in Eq. (42). Rosenfeld and Ashcroft[13] proved that the bridge function in a classical liquid is almost independent of an interatomic potential and that it can be approximated by the bridge function of a hard-core fluid with the proper choice of the hard-sphere diameter. Following their theory, here we make the approximation to the bridge function of the two-component system:

$$B_{I\text{-}I}(r) \simeq B_{\mathrm{PY}}(r,\eta) \ , \tag{46}$$

where $B_{\mathrm{PY}}(r,\eta)$ is that of Percus-Yevick equation for the hard spheres of diameter σ and density $n_0 \equiv n_0^I = n_0^e$ with the packing fraction $\eta \equiv \pi n_0 \sigma^2/6$. On the other hand, in a liquid metal the electron-ion correlation is not so strong that we have neglected the bridge function $B_{e\text{-}I}(r)$ between electron and ion in Eq. (42). In the usual treatment, the exchange-correlation effect of electrons in liquid and solid metals is assumed to be equal to that of the jellium model; that is, the influence of ions on the electrons is neglected, and the ions are replaced by the uniform positive charge in the jellium model. On the basis of this model we can use an approximate expression for the local-field correction (LFC) $G(Q)$ for electrons in a liquid metal using the LFC $G^{\mathrm{jel}}(Q)$ of the jellium model

$$G(Q) \simeq G^{\mathrm{jel}}(Q) \ , \tag{47}$$

where the LFC is defined by

$$C_{e\text{-}e}(Q) \equiv -\beta v_{e\text{-}e}(Q)[1-G(Q)] \ . \tag{48}$$

In our calculation, we use the LFC proposed by Geldard and Vosko[14] for $G^{\mathrm{jel}}(Q)$, which is written as

$$G_{e\text{-}e}^{\mathrm{jel}}(Q) = \frac{q^2}{2q^2+4g} \tag{49}$$

with

$$g = 1/(1+0.0155\alpha\pi r_s) \ , \tag{50}$$

and $q \equiv Q/Q_F$ and $\alpha \equiv (\frac{4}{9}\pi)^{1/3}$. The local-density approximation for the exchange-correlation potential in Eq. (33) is taken to be of the form proposed by Gunnarsson and Lundqvist:[15]

$$\mu_{\mathrm{xc}}(r_s) = -\frac{2}{\pi\alpha r}[1+0.0545 r_s \ln(1+11.4/r_s)] \ \mathrm{Ry} \ . \tag{51}$$

Under these two approximations, (46) and (47), Eqs. (41) and (42) combined with the electron-ion interaction (33) constitutes a set of integral equations for calculating $C_{I\text{-}I}(r)$ and $C_{e\text{-}I}(r)$ self-consistently, with η remaining as a parameter to be determined by some condition.

The atomic number of lithium is $Z_A=3$ and its ionic valency in a liquid state is $Z_I=1$; two electrons are bound in the 1*s* orbital. States of the liquid metallic lithium can be specified by the two parameters, the plasma parameter $\Gamma \equiv \beta e^2/a$ and $r_s \equiv a/a_B$, where the average spherical radius a is defined by $(3/4\pi n_0)^{1/3}$ and a_B is the Bohr radius. Because of a large plasma parameter $\Gamma \simeq 200$ and large $r_s \simeq 3$ of this system, it is difficult to solve iteratively these integral equations when applied to a liquid metallic lithium. Therefore we can obtain the convergent solution for this system, only when initial values for $C_{I\text{-}I}(r)$ and $C_{e\text{-}I}(r)$ used in the iteration process can be chosen properly. Let us imagine that we position ourselves at a nucleus at the origin and assume that the ion distribution $g_{I\text{-}I}(r)$ around it is already known. The bound- and valence-electron distributions around the nucleus at the origin depend on the ion distribution $g_{I\text{-}I}(r)$ which we suppose to be given at the beginning. Inversely, the interatomic pair interaction which determines the ion-ion RDF $g_{I\text{-}I}(r)$ depends on how valence electrons are accumulated, $n_e^v(r|N)$, and also on how many electrons are bound around it, $n_e^b(r|N)$; hence, the electron distribution must be self-consistent with $g_{I\text{-}I}(r)$. Therefore it is important to set up the pair interaction determining $g_{I\text{-}I}(r)$ and the electron density distributions $[n_e^b(r|N)$ and $n_e^v(r|N)]$ as close to the real ones as possible in the choice of the first guesses used in the iteration solving Eqs. (41) and (42) with (46) and (47). Considering this fact, we take the following three steps to solve the integral equations.

In the first step, we use the jellium-vacancy model to obtain initial input data, i.e., the RDF $g_{I\text{-}I}(r)$ is approximated by the step function $\Theta(R-r)$:

$$g_{I\text{-}I}(r)\simeq\Theta(R-r)=\begin{cases}0 & \text{for } r<R\,,\\ 1 & \text{for } r>R\,,\end{cases} \tag{52}$$

with R being the Wigner-Seitz radius, and the DCF $C_{e\text{-}I}(r)$ in Eq. (32) being approximated by the Coulomb potential $\beta Z_I e^2/r$ between electron and ion. These approximations to Eqs. (41) and (42) lead to the same problem in determining the electron distribution around a lithium nucleus fixed at the center of vacancy in the jellium. This system generates the potential for electrons caused by a charge Z_A fixed at the center of the jellium vacancy in the form

$$v_{e\text{-}I}^{\text{eff}}(r)=\tilde{v}_{e\text{-}I}(r)+f(r)-\overline{\Gamma}_{e\text{-}I}(r)/\beta, \tag{53}$$

with the definition of new functions

$$\overline{\Gamma}_{e\text{-}I}(r)\equiv\int C_{e\text{-}e}^{\text{jel}}(|\mathbf{r}-\mathbf{r}'|)\delta n_e^v(r')d\mathbf{r}'\,, \tag{54}$$

$$f(r)\equiv\begin{cases}Z_I e^2[3-(r/R)^2]/2R & \text{for } r<R\,,\\ Z_I e^2/r & \text{for } r>R\,.\end{cases} \tag{55}$$

The integral equation for $C_{e\text{-}I}(r)$ described by Eq. (42) in this approximation is rewritten in the form of the equation for $\overline{C}_{e\text{-}I}(r)$:

$$\hat{B}\,\overline{C}_{e\text{-}I}(r)=n_e^{0v}(r|\tilde{v}_{e\text{-}I}+f-\overline{\Gamma}_{e\text{-}I}/\beta)/n_0^e-1-\hat{B}\,\overline{\Gamma}_{e\text{-}I}(r)\,. \tag{56}$$

Because of the relation derived by the Fourier transforms of Eqs. (54) and (56),

$$\overline{\Gamma}_{e\text{-}I}(Q)=\frac{n_0^e C_{e\text{-}e}^{\text{jel}}(Q)\overline{C}_{e\text{-}I}(Q)/\beta}{1-n_0^e C_{e\text{-}e}^{\text{jel}}(Q)\chi_Q^0}\,, \tag{57}$$

Eq. (56) constitutes an integral equation for $\overline{C}_{e\text{-}I}(r)$. Once $\overline{C}_{e\text{-}I}(r)$ is obtained from Eq. (56), the DCF $C_{e\text{-}I}(Q)$ which appears in the pair interaction (11) is calculated from the relation

$$C_{e\text{-}I}(Q)=\overline{C}_{e\text{-}I}(Q)+3\beta\frac{4\pi Z_I e^2}{Q^2}\,\frac{\sin(RQ)-RQ\cos(RQ)}{(RQ)^3}\,. \tag{58}$$

In the second step, we notice that Eq. (41) with (46) can be rewritten in the form of the integral equation for the DCF $C(r)$ in one-component fluid as is shown by Eq. (12):

$$\begin{aligned}C(r)&\equiv C_{I\text{-}I}(r)-\kappa(r)\\ &=\exp[-\beta v^{\text{eff}}(r)+\gamma(r)+B_{\text{PY}}(r,\eta)]-1-\gamma(r)\,,\end{aligned} \tag{59}$$

where

$$\mathcal{F}_Q[\kappa(r)]\equiv|C_{e\text{-}I}(Q)|^2\frac{n_0^e\chi_Q^0}{1-n_0^e C_{e\text{-}e}^{\text{jel}}(Q)\chi_Q^0}\,, \tag{60}$$

and

$$\gamma(r)\equiv n_0^I\int C(|\mathbf{r}-\mathbf{r}'|)[g_{I\text{-}I}(r')-1]d\mathbf{r}'\,. \tag{61}$$

This equation is the modified HNC equation[13] for one-component fluid with an interatomic potential $v^{\text{eff}}(r)$ determined by $w_b^{\text{nl}}(r)\equiv -C_{e\text{-}I}(r)/\beta$ using Eq. (11). Therefore, we can calculate an approximate $g_{I\text{-}I}(r)$ by using $v^{\text{eff}}(r)$, which is generated from the $C_{e\text{-}I}(Q)$ of the jellium-vacancy model in the first step.

In the third step, Eq. (42) is taken as a closed integral equation for $C_{e\text{-}I}(r)$, $n_e^b(r|N)$, and $n_e^v(r|N)$, with the use of $g_{I\text{-}I}(r)$ obtained in the second step, since $C_{I\text{-}I}(r)$ and $C_{e\text{-}e}^{\text{jel}}(r)$ are now known functions. In this step, we can evaluate new $C_{e\text{-}I}(Q)$ and $n_e^b(r|N)$ by using the results ($C_{e\text{-}I}$, n_e^b, and n_e^v) of the first step as initial data in the iteration. After some repetitions of the second and third steps, we can obtain initial guesses to $C_{I\text{-}I}(r)$, $C_{e\text{-}I}(r)$, and $n_e^b(r)$, which are used to finally solve a set of integral equations (41) and (42) determining $C_{I\text{-}I}(r)$, $C_{e\text{-}I}(r)$, $n_e^b(r|N)$, and $n_e^v(r|N)$ in a self-consistent manner. In solving these integral equations by the iterative method, we must use the procedure to avoid the divergence due to the long range of the Coulomb force [for details, see Ref. 7(a)]. In this way, we have solved a set of integral equations for liquid metallic lithium at two temperatures 470 and 595 K and compared it with the experimental results of Olbrich, Ruppersberg, and Steeb;[16] the parameter η involved in the hard-sphere bridge function is chosen so as to yield the experimental values of $S_{I\text{-}I}$ (0) by the calculations.

In the first place, the structure factor $S_{I\text{-}I}(Q)$ is calculated at temperatures of 470 K, which is near its melting point 453.7 K. At this temperature, the number density is 4.45×10^{-2} atoms Å^{-3}, which gives the plasma parameter $\Gamma=203.1$ and $r_s=3.308$. The parameter η contained in the bridge function is chosen as 0.48, which yields $S_{I\text{-}I}(0)=3.15\times10^{-2}$, while the experimental value is 3.06×10^{-2} (Ref. 16). In Fig. 1, the solid curve is the

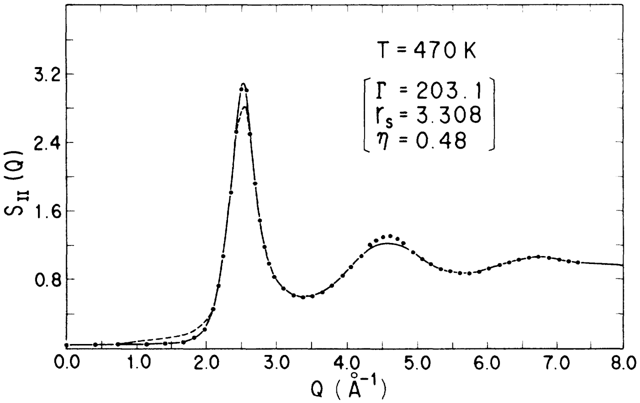

FIG. 1. Ion-ion structure factors for Li at 470 K; the calculated $S_{I\text{-}I}(Q)$ (solid circles) is compared with those observed by the neutron diffraction (solid curve) and x-ray diffraction (dashed curve) experiments performed by Olblich *et al.*

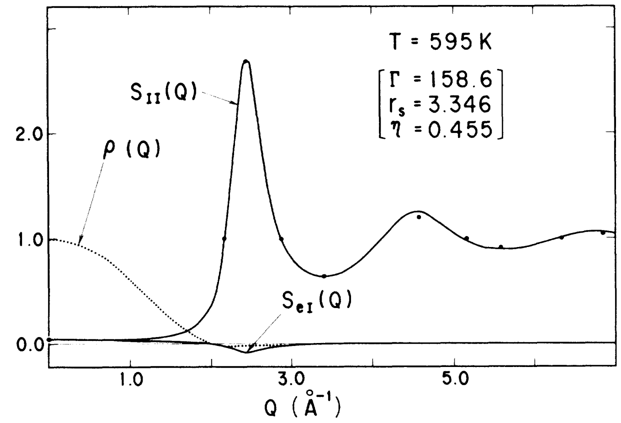

FIG. 2. Ion-ion and electron-ion structure factors for Li at 595 K; the solid curves indicate the calculated result in comparison with experiment (solid circles). The dotted curve is the Fourier transformed density distribution of a neutral pseudoatom, which has the relation $S_{e\text{-}I}(Q)=\rho(Q)S_{I\text{-}I}(Q)$.

structure factor $S_{I\text{-}I}(Q)$ observed by Olbrich, Ruppersberg, and Steeb[16] by means of the neutron diffraction and the solid circles are the result of this calculation with the use of the above parameters, while the dashed curve is that observed by the x-ray diffraction. The agreement between the theory and the experiment is excellent except near the second peak. The difference between the neutron and x-ray experiments may be attributed to the improper treatment of the valence electrons in the analysis to extract the structure factor from x-ray data.[17]

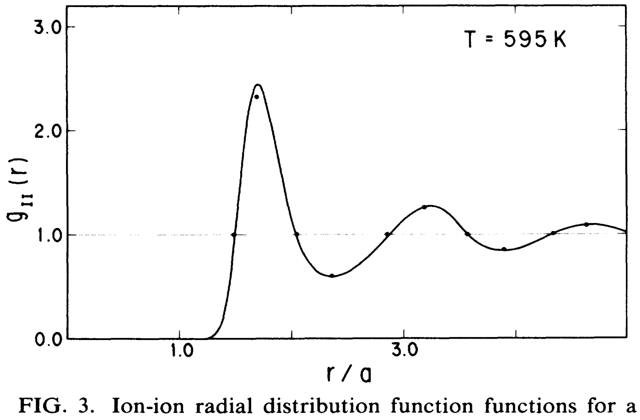

FIG. 3. Ion-ion radial distribution function functions for a liquid lithium at 595 K obtained by the present calculation (solid curve) and by the experiment (solid circles).

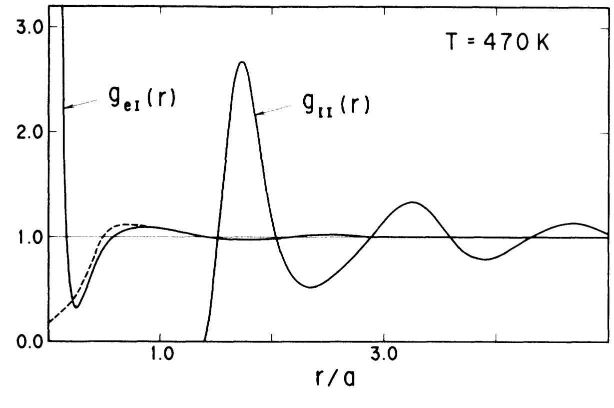

FIG. 4. Ion-ion and electron-ion radial distributions evaluated by the present integral equations (solid curves) at 470 K; the dashed curve is obtained by the use of the linear-response formula with the Ashcroft pseudopotential.

Next, we have calculated the electron-ion and ion-ion structure factors at a temperature of 595 K shown by the solid curves in Fig. 2; the solid circles are the experimental result of the neutron diffraction. The electron-ion correlation is very weak. The Fourier transform of valence-electron distribution $\rho(Q)$ of the pseudoatom is obtained from $S_{e\text{-}I}(Q)$ using the relation (16); the result is shown in Fig. 2 by the dotted curve. In Fig. 3, the calculated RDF (the solid curve) at this temperature is compared with that extracted from experimental data, which is plotted by the solid circles. The structure factor $S_{I\text{-}I}(Q)$ and RDF $g_{I\text{-}I}(r)$ obtained from our integral equations show quite good agreement with the experimental results also at this temperature. In Fig. 4, the electron-ion and ion-ion RDF's at 470 K are shown in conjunction with the dashed curve, which denotes the electron-ion RDF calculated from Eq. (16) with the replacement of $C_{e\text{-}I}(Q)$ by $-\beta w_b(Q)$, the Fourier transform of Ashcroft's pseudopotential with the core radius $r_c=0.74$ Å, that is, equivalent to $g_{e\text{-}I}(r)$ obtained by the linear-response formula with the use of $w_b(r)$. The dip in $g_{e\text{-}I}(r)$ near $0.25a$ in the core region is caused by the Pauli principle that requires the valence wave function to be orthogonal to the 1s orbital of the core electrons. Thus we can see that the pseudopotential treatment gives a fairly good description of $g_{e\text{-}I}(r)$ outside the core region, but cannot describe correctly the behavior of valence electrons near the origin. Here, it should be noted that the RDF $g_{e\text{-}I}(r)=n_e^v(r)/n_0$ does not contain the part of the bound-electron distribution $n_e^b(r)$ around the central nucleus, which fills up the dip in $g_{e\text{-}I}(r)$ in Fig. 4.

The valence-electron distribution of the pseudoatom $\rho(r)$ and the bound-electron distribution $n_e^b(r|N)$ at a temperature of 470 K are displayed in Fig. 5, where the density is normalized by the uniform density n_0; $n_e^b(r|N)$ is quite the same as the density distribution $\rho_{1s}(r)$ of 1s electrons in a free atom and therefore is displayed by the same curve as $\rho_{1s}(r)$. The dotted curve in Fig. 5 is $\rho(r)$ calculated by the linear-response formula with the Ashcroft pseudopotential. It is interesting to note that $\rho(r)$ of the pseudoatom in a liquid metal shows a behavior quite similar to the 2s-electron-density distribution $\rho_{2s}(r)$ of a free atom except that the former has negative parts in the large distances. In spite of the fact that the 2s electrons are spread out uniformly in a liquid metallic lithium, we can redistribute the valence electron $\rho(r)$ to each ion, and think of a liquid metal as consisting of neutral atoms with the charge distribution:

$$\rho_{\text{pa}}(r)\equiv n_e^b(r)+\rho(r)\simeq\rho_A(r)\equiv\rho_{1s}(r)+\rho_{2s}(r)\ , \qquad (62)$$

which is almost equal to the total atomic electron distri-

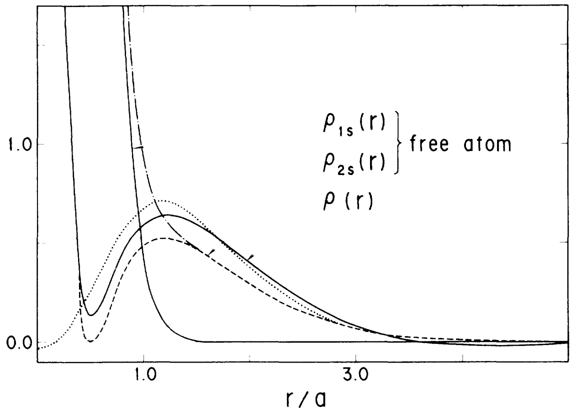

FIG. 5. Charge distributions of a neutral pseudoatom in a liquid lithium at 470 K, compared with those of a free atomic Li. The 1*s*-electron distribution $n_e^b(r|N)$ of the neutral pseudoatom is indistinguishable from the density $\rho_{1s}(r)$ of the free atom plotted by the solid curve, while the valence 2*s*-electron density shows a distinct but similar behavior when compared between the pseudoatom $\rho(r)$ and the free atom $\rho_{2s}(r)$, which are displayed by the dashed and solid curves, respectively. The total charge distribution of the free atom is shown by the solid curve with dots. The dotted curve denotes the valence-electron distribution of the pseudoatom evaluated by the linear-response formula with the Ashcroft pseudopotential. Here, density distributions are normalized by the uniform density n_0.

bution $\rho_A(r)$ of Li denoted by the solid curve with dots in Fig. 5. Thus we can understand from Fig. 5 that this neutral pseudoatom model of Ziman[10] is valid irrespective of the strength of the electron-ion interaction, i.e., without use of the linear-response formula.

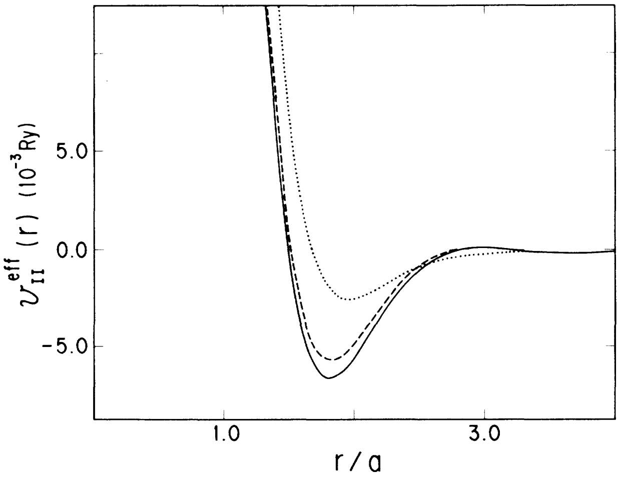

FIG. 6. Effective interatomic potentials for a liquid lithium at 470 K, obtained by the full self-consistent calculation (solid curve) and by the use of jellium-vacancy model (dashed curve). The dotted curve denotes the interatomic potential calculated by the usual pseudopotential theory using the Ashcroft potential with $r_c = 0.74$ Å.

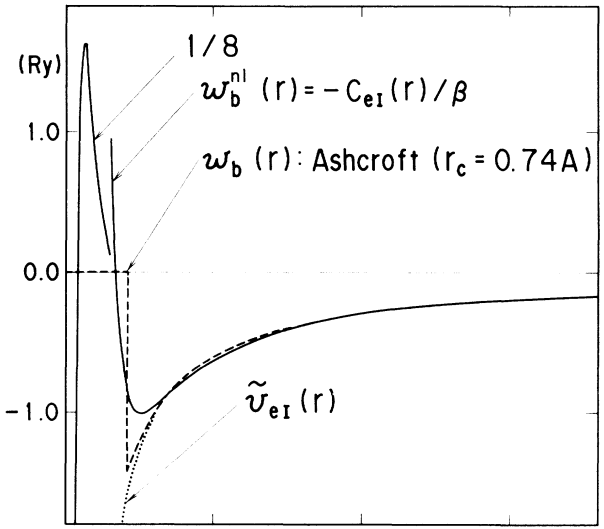

FIG. 7. Electron-ion direct correlation function, which plays the role of the nonlinear pseudopotential, in comparison with the Ashcroft potential (dashed curve). Near the origin, $w_b^{\text{nl}}(r)$ is displayed in the reduced scale with $\frac{1}{8}$. The electron-nucleus interaction $\tilde{v}_{e\text{-}I}(r)$ is shown by the dotted curve.

The point of success in this calculation is in the fact that the effective interatomic interaction $v^{\text{eff}}(r)$ is determined in a self-consistent manner with the core-electron states and the ionic configuration, without use of any information other than the atomic number Z_A. The interatomic pair potential at a temperature of 470 K is plotted by the solid curve in Fig. 6; the dashed curve is that obtained by the use of the jellium-vacancy model in the first step, while the dotted curve is the pair potential based on the Ashcroft model potential. The procedure for determining $v^{\text{eff}}(r)$ on the basis of the jellium-vacancy model in the first step is essentially the same as that of Dagens, Rasolt, and Taylor[18] (DRT), who introduced a nonlocal pseudopotential with some parameters, which are determined so as to take account of nonlinear effects in the screening. It is important to notice that in our formulation we need not use a nonlocal pseudopotential; instead of that, the electron-ion DCF $w_b^{\text{nl}}(r) \equiv -C_{e\text{-}I}(r)/\beta$ plays the role of a pseudopotential, which takes account of the nonlinear screening in the form of a local pseudopotential. This nonlinear pseudopotential is displayed by the solid curve in Fig. 7, which is to be compared with the Ashcroft model potential denoted by the dashed curve. The pseudopotential $w_b^{\text{nl}}(r)$ becomes negative near the origin due to the attraction of the nucleus, but the behavior of $w_b^{\text{nl}}(r)$ in this region is not so important in playing the role of pseudopotential; in the DRT treatment the steep variation near the $\rho(r)$ is replaced by a smoother curve. The bare electron-ion interaction $\tilde{v}_{e\text{-}I}(r)$ given by Eq. (33) is close to the DCF outside the region of $r \simeq 0.6a$, where the RPA $C_{e\text{-}I}(r) \simeq -\beta \tilde{v}_{e\text{-}I}(r)$ is valid, as is displayed in Fig. 7 by the dotted curve.

IV. CONCLUDING REMARKS

By applying our formulation based on the nucleus-electron model to the liquid metallic lithium, we have shown that the electron-ion and ion-ion RDF's in a liquid metal can be calculated with the use of the atomic number Z_A as the only input data. It is important to remind the reader that the RDF $g_{e\text{-}I}(r)$ contains the information for the electron cloud $\rho(r)$ of the pseudoatom, as shown by Eq. (16), and the electron cloud $\rho(r)$ leads to giving the nonlinear pseudopotential $w_b^{\text{nl}}(r) \equiv -C_{e\text{-}I}(r)/\beta$ which yields the interatomic pair potential $v^{\text{eff}}(r)$ by Eq. (11); finally the RDF $g_{I\text{-}I}(r)$ is obtained by this pair potential. Consequently, the RDF $g_{e\text{-}I}(r)$, the electron cloud $\rho(r)$, and the pseudopotential $-C_{e\text{-}I}(r)/\beta$ can be regarded as determined in a self-consistent way to agree with the experimental $S_{I\text{-}I}(Q)$, since the structure factor $S_{I\text{-}I}(Q)$ is calculated from the pair interaction $v^{\text{eff}}(r)$ based on these quantities and shows quite good agreement with the experimental result as shown in Figs. 1 and 2.

In our formulation the liquid structure of a liquid metal is always described by a pair interaction, i.e., we need not introduce many-body forces such as a three-body one, provided that a liquid metal can be considered as a binary mixture of ions and electrons. The reason why the description of a liquid metal by a pair interaction is always possible is that in our formulation we can calculate such a pseudopotential as is self-consistent with the ion configuration $g_{I\text{-}I}(r)$ and takes account of the nonlinear screening around a nucleus; the DCF $-C_{e\text{-}I}(r)/\beta$ plays the role of a "nonlinear" pseudopotential as was discussed by DRT.[18] Furthermore, it is important to note that we need not use a nonlocal form of the pseudopotential. Also, the neutral pseudoatom model proposed by Ziman[10] is shown, in terms of the DCF $-C_{e\text{-}I}(r)/\beta$, to exactly hold for any liquid metal taken as an ion-electron mixture, irrespective the strength of the electron-ion interaction.

In the present calculation the parameter η of the hard-sphere bridge function was determined so that the solution of the modified HNC equation would yield $S_{I\text{-}I}(0)$, in agreement with the experimental value. Alternatively this parameter may be determined without use of the experimental result by the requirement of the thermodynamic self-consistency which states that the virial and compressibility equation should lead to the same isothermal compressibility as a one-component system with a pair interaction (11):

$$\frac{\partial(\beta P_v)}{\partial n_0} = \frac{1}{S_{I\text{-}I}(0)} , \tag{63}$$

with the virial pressure

$$\beta P_v = n_0 - \frac{\beta}{6} n_0^2 \int d\mathbf{r}\, r \frac{dv^{\text{eff}}(r)}{dr} g_{I\text{-}I}(r) . \tag{64}$$

In this expression, the dependence of the pair interaction on the density need not be taken into account, since we replace the problem, to determine the RDF $g_{I\text{-}I}(r)$ in the two-component system, by that in the equivalent one-component system with the fixed pair interaction (11), which yields the same RDF to $g_{I\text{-}I}(r)$ in the ion-electron mixture as was described by Eq. (59). The above procedure may give almost the same values for the parameter η as given by in Sec. III, since our condition determining η there is of essentially the same character as this one.

In the present calculation electrons in a liquid metal are treated as in a fully degenerate states because of their high Fermi temperature. But our formulation can be applied to a high-density plasma where electrons behave as a fluid at absolute zero to temperatures so high as to become a classical fluid. Therefore our formulation, which can provide a temperature-dependent pseudopotential, can be expected to give a good description of plasmas, since it is proved that the liquid structure can be calculated in excellent agreement with the experimental result by this method. It is interesting to see that the pseudopotential determined by the jellium-vacancy model, as mentioned in Sec. III, gives the interatomic pair potential $v^{\text{eff}}(r)$, in fair agreement with that of the full calculation as shown in Fig. 6. This fact suggests that we can also obtain a temperature-dependent pseudopotential for a high-density and high-temperature plasma on the basis of the jellium-vacancy model as the full approximation.

It is of interest that the valence-electron density $\rho(r)$, including nonlinear screening, is given by the form of the linear-response formula for an electron gas in the jellium model with the use of $-C_{e\text{-}I}(Q)/\beta$ as an electron-ion interaction:

$$\rho(Q) = n_0^e C_{e\text{-}I}(Q) \chi_Q^{\text{jel}} . \tag{65}$$

Moreover, it should be pointed out that this nonlinear pseudopotential $-C_{e\text{-}I}(Q)/\beta$ can yield precisely the density distribution near the origin, where the usual pseudopotential theory does not work well; Fig. 5 indicates this fact. Furthermore, it should be remembered that Eq. (65), although taking a linear-response expression, does not contain the contribution of bound electrons around the nucleus. If we use the Ashcroft model potential $w_b(Q)$ in the place of $-C_{e\text{-}I}(Q)/\beta$, the linear-response formula (65) enables us to give the density $\rho(r)$ in a fairly good approximation, except near the origin, as is shown in Fig. 5, since the Ashcroft potential excludes the bound-electron contribution to $\rho(r)$. However, if we use the RPA $C_{e\text{-}I}(r) \simeq \beta \bar{v}_{e\text{-}I}(r)$ replaced by the bare electron-nucleus potential or the approximation $C_{e\text{-}I}(r) \simeq \beta Z_I e^2/r$, the bare-electron-ion Coulomb interaction, the density $\rho(r)$ given by the linear-response formula (65) involves the contribution of bound states to some extent, which must not be contained in the valence-electron part $\rho(r)$. Hence it may yield a very bad result for the valence-electron density $\rho(r)$ in the pseudoatom. For the same reason as mentioned above, the method proposed by Dharma-wardana and Perrot[19] to treat a high-density plasma may not be applied to a liquid metal, since their approach involves the approximation $C_{e\text{-}I}(r) \simeq \beta Z_I e^2/r$ in the expression for $v_{e\text{-}I}^{\text{eff}}(r)$ given by Eq. (32), which leads approximately to the interatomic pair interaction (11) with the replacement of $C_{e\text{-}I}(Q)$ by $4\pi\beta Z_I e^2/Q^2$; this brings about the contribution of the bound electron to $\rho(r)$. Accordingly, it is also inappropriate to apply their method to a plasma when the bound-electron contribution is not negligible.

In the present paper, we have represented only the result for the structure as a liquid. Our formulation can determine the liquid structure, consistent with the atomic structure of an ion in a liquid metal. Therefore, it is another important test of our formulation to examine whether it can give a proper spectroscopic calculation of the bound levels of the ion. The method of Slater's transition state[20] based on our integral equations gives the value of 51.5 eV for the K edge of Li, which is caused by the $1s$ bound electron around the ion in a liquid metallic state, while 51.3 eV is an observed value for a liquid metallic lithium at 490 K by the soft-x-ray experiments. The details of this calculation are reserved for another paper.

The next work is to ascertain how extensively our formulation is applicable in substances other than liquid metallic lithium; the structure of simple metals such as Na may be calculated by this formulation without difficulty. Also, it is easy to extend this formulation to the case of a binary alloy.

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