Space-Time Correlation Functions in Quantal and Classical Binary Mixtures. II

—— *Liquid Metals as Coupled Electron-Ion Systems*[*] ——

Junzo CHIHARA

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11

The method developed previously for calculating the correlations in quantal binary mixtures is applied to liquid metals which are considered as mixtures of classical particles (ions) and quantal particles (electrons); as a result, the dynamic and static structure factors as well as the radial distribution functions of ions, ion-electrons and electrons are calculated on the basis of model potentials with the use of the parameters appropriate to Na. The ion-ion structure factor is similar to that of the Percus-Yevick hard-sphere model except that the first peak is shifted to the small wave-number side and distorted in an asymmetrical form. The ion-electron correlation is shown to be very small; thus, the radial distribution function of electrons almost coincides with that calculated from the jellium model. It is important to introduce quantal direct correlation functions, in terms of which we can represent the compressibility of a liquid metal, including the Bohm-Staver term, and that of a fused salt in a unified manner; and the effective direct correlation function of ions in the one-component model for liquid metal can also be defined by using these quantal direct correlation functions. The Friedel sum rule is extended to the case of the electron density distribution around a constituent ion in a liquid metal; hence, we can also show the distortion of the electron density distribution around each ion to be small. We may conclude that the ions in a simple liquid metal are moving around without disturbing the uniform density distribution of the electron gas, which behaves as if in the jellium model.

§ 1. Introduction

So far, liquid metals have been treated as one-component systems in usual theoretical work on static or dynamical structures of ions, and the presence of conduction electrons has been taken into account only through the construction of the effective ion-ion potentials. However, it may be a matter of great interest to investigate the conduction electrons themselves on the same footing as the ions by treating liquid metals as coupled electron-ion systems; thus, we are able to clarify the limit of the approach through effective potentials and to throw light on the novel aspects of electron-ion systems.

Earlier work by Cowan and Kirkwood[1] is an attempt to calculate the radial distribution functions (RDF) in liquid metals on the basis of the two-component model. However, their procedure is not applicable to real liquid metals at normal

---

[*] Some preliminary results of the present paper were reported at the Second International Conference on "The Properties of Liquid Metals" held at Tokyo, 1972.

temperatures since they treated the ions with the Debye-Hückel approximation and the electrons with the Thomas-Fermi method. Recently there have also been developed several theories[2]~[7] to investigate the dynamical structure of liquid metals in the zero sound wave region from this model, but these treatments cannot afford to calculate the RDF of ion-ion, ion-electron and electron-electron, namely, $g_{II}(r)$, $g_{Ie}(r)$ and $g_{ee}(r)$ in liquid metals.

In a previous preliminary work,[8] we have presented a method of calculating the static and dynamic structure factors of liquid metals as mixtures of ions and electrons in a self-consistent manner, where integral equations are used for $g_{ij}(r)$ in an ad hoc way without derivation. Since then, we have derived various types of integral equations of liquid structures in quantal mixtures by extending Percus' functional-expansion method to quantal systems.[9] In the present paper, we investigate the behaviour of the ions and the electrons in liquid metals with the use of these results.

Very recently, Egelstaff et al.[10] have proposed to extract the electronic correlations in liquid metals by combining neutron, X-ray and electron scattering data. In the near future, the behaviour of the electronic correlations such as $g_{eI}(r)$ and $g_{ee}(r)$ in liquid metals will be clarified from both theoretical and experimental points of view.

In § 2 we give a summary and supplement of the previous results for quantal mixtures.[9] In § 3 on making use of the results in § 2, some general results in a liquid metal are derived, including its compressibility and the Friedel sum rule for the electron density distribution around a constituent ion in the liquid metal. We calculate the static and dynamic structure factors and also the RDF by solving an integral equation numerically with the use of model potentials in § 4. In the last section, we discuss the important role of the quantal direct correlation functions (DCF) in treating a liquid metal and construct a physical picture of simple liquid metals.

§ 2. Previous results and supplement

In a previous paper[9] (hereafter referred to as I), on the basis of a generalized Hartree approximation,[11] we have introduced the quantal DCF $\widetilde{C}_{ij}(r)$ for binary mixtures in the form

$$\mathcal{F}_Q\{(n_i n_j)^{1/2}\widetilde{C}_{ij}(r)\} = \frac{1}{\chi_Q^{0i}}\delta_{ij} - (n_i n_j)^{1/2}\mathcal{F}_Q\left\{\frac{\delta[-\beta U_i(r)]}{\delta n_j(r')}\right\} \qquad (2\cdot1)$$

$$= \frac{1}{\chi_Q^{0i}}\delta_{ij} - (-)^{i+j}\chi_Q^{\bar{i}\bar{j}}/\{\chi_Q^{11}\chi_Q^{22} - \chi_Q^{12}\chi_Q^{21}\}, \qquad (2\cdot2)^{*)}$$

$$\mathcal{F}_Q[f(r)] \equiv \int f(r)e^{iQr}d\boldsymbol{r}. \qquad (2\cdot3)$$

---

*) This equation corresponds to Eq. (2·21) of I, which was miswritten: $\beta v_{ij}(Q)$ of I must be defined as $\beta v_{ij}(Q) = -\widetilde{C}_{ij}(Q)$, using $\widetilde{C}_{ij}(Q)$ in this paper.

Here, n_i is the average number of particles of species i; χ_Q^{ij} represents the density-density canonical correlation which reduces to the structure factor $S_{ij}(Q)$ in the classical limit; $\bar{i}$ denotes the component of a type different from i; and χ_Q^{0i} the density-density canonical correlation of the corresponding non-interacting system.

On the other hand, in classical binary mixtures, when one imposes external potentials $U_i(r)$ upon i-species particles in the mixture, and sets these external potentials equal to their interatomic potentials $v_{ij}(r)$ in such a way as $U_1(r) = v_{1j}(r)$ and $U_2(r) = v_{2j}(r)$, there follow the general relations[12] between the i-component density distribution $n_i(r|U_1 = v_{1j}, U_2 = v_{2j}) \equiv n_i(r|j)$ and the DCF $C_{ij}(r)$:

$$\sum_k \int \frac{\delta[-\beta U_i(r)]}{\delta n_k(r')}\Big|_0 \{n_k(r'|j) - n_k\}\, dr' = C_{ij}(r). \tag{2·4}$$

Here, β is the inverse temperature, $|_0$ denotes the functional derivative being taken at $n_k(r) = n_k$. It should be noted that $n_i(r|j)$ denotes the i-species density distribution around a fixed j-species particle at the origin since the imposition of the external potentials $U_k = v_{kj}$ is equivalent to fixing a j-species particle at the origin. At this point, by making the ansatz that the above relation (2·4) remains valid even in quantal mixtures only if we replace the classical quantities by their quantal analogs, we obtain the Fourier transform of $n_i(r|j)$ in quantal mixtures as follows:

$$\left(\frac{n_j \chi_Q^{0j}}{n_i \chi_Q^{0i}}\right)^{1/2} \cdot \mathscr{F}_Q[n_i(r|j) - n_i] = \frac{\chi_Q^{ij}}{(\chi_Q^{0i}\chi_Q^{0j})^{1/2}} - \delta_{ij}, \tag{2·5}$$

$$\equiv (n_i n_j)^{1/2}\mathscr{F}_Q[\tilde{g}_{ij}(r) - 1]. \tag{2·6}*$$

From Eq. (2·5), it follows that

$$\chi_Q^{01} \cdot \mathscr{F}_Q\left[\frac{n_2(r|1)}{n_2} - 1\right] = \chi_Q^{02} \cdot \mathscr{F}_Q\left[\frac{n_1(r|2)}{n_1} - 1\right], \tag{2·7}$$

which means that the symmetrical relation in a classical mixture, $n_2(r|1)/n_2 = n_1(r|2)/n_1$, becomes no longer valid in the case of a quantal mixture. In this respect, it should be mentioned that the linear response result for $\mathscr{F}_Q\{n_i(r|j)/n_i - 1\}$ is consistent with the general relation (2·7), that is, Eq. (2·7) can be proved to be satisfied, at least, for mixtures interacting via weak interatomic potentials.

In addition, we have obtained the density-density response functions in terms of the quantal DCF as follows:

$$\chi_Q^{ii}(\omega) = \chi_Q^{0i}(\omega)\varepsilon_{\bar{i}}(Q,\omega)/\bar{\varepsilon}(Q,\omega). \tag{2·8}**$$

$$\beta\chi_Q^{i\bar{i}}(\omega) = (n_i n_{\bar{i}})^{1/2}\widetilde{C}_{i\bar{i}}(Q)\chi_Q^{0i}(\omega)\chi_Q^{0\bar{i}}(\omega)/\bar{\varepsilon}(Q,\omega) \tag{2·9}***$$

where

---

*) Eq. (2·42) of I.
**) Eq. (2·33) of I.
***) Eq. (2·34) of I.

$$\bar{\varepsilon}(Q,\omega) \equiv \varepsilon_1(Q,\omega)\,\varepsilon_2(Q,\omega) - n_1 n_2 \{\widetilde{C}_{12}(Q)\}^2 \chi_Q^{\,01}(\omega)\,\chi_Q^{\,02}(\omega), \qquad (2\cdot10)$$

$$\varepsilon_i(Q,\omega) \equiv 1 - n_i \widetilde{C}_{ii}(Q)\,\chi_Q^{\,0i}(\omega), \qquad (2\cdot11)$$

and $\chi_Q^{\,0i}(\omega)$ is the free-particle polarizability of component i. In these expressions the density-density canonical correlations $\chi_Q^{\,ij}$ remain undetermined.

In order to evaluate $\chi_Q^{\,ij}$ we have derived several integral equations for $n_i(r|j)$ by extending Percus' method to be applicable to quantal mixtures. As a first example, we have obtained a quantal hypernetted chain equation for mixtures, which is written as

$$n_i(r|j) = n_i^{\,0}(r|v_{ij}^{\,H}) \qquad (2\cdot12)$$

with

$$v_i^{\,H}(r) \equiv v_{ij}(r) - \sum_l \frac{1}{\beta} \int \widetilde{C}_{il}(|\boldsymbol{r}-\boldsymbol{r'}|)\,\{n_l(r'|j) - n_l\}\,d\boldsymbol{r'}, \qquad (2\cdot13)$$

where $n_i^{\,0}(r|u)$ is defined by

$$n_i^{\,0}(r|u) \equiv \sum_{\boldsymbol{k}} n_{\boldsymbol{k}}^{\,i}\,|\phi_{\boldsymbol{k}}^{\,i}(\boldsymbol{r})| \qquad (2\cdot14)$$

in terms of the solution $\phi_{\boldsymbol{k}}^{\,i}(\boldsymbol{r})$ of the wave equation in the presence of an external potential u:

$$\left\{ -\frac{\hbar^2}{2m_i}\boldsymbol{\nabla}^2 + u(r) \right\}\phi_{\boldsymbol{k}}^{\,i}(\boldsymbol{r}) = E_{\boldsymbol{k}}\phi_{\boldsymbol{k}}^{\,i}(\boldsymbol{r}), \qquad (2\cdot15)$$

and $n_{\boldsymbol{k}}^{\,i}$ denotes the distribution function of component i. That is, $n_i^{\,0}(r|u)$ denotes the i-species particle density distribution in the presence of an external potential u in the case where i-species particles have no interaction with each other. In a second example, by dividing the bare interatomic potentials v_{ij} into the weak long-range part $v_{ij}^{\,L}$ and the strong short-range part $v_{ij}^{\,S}$, we have obtained an integral equation appropriate to charged mixtures in the form

$$\boldsymbol{\nabla}\widetilde{C}_{ij}(r) = -\boldsymbol{\nabla}\big[(\hat{B}_i \hat{B}_j)^{-1/2}\tilde{g}_{ij}(r)\,\{1/\tilde{g}_{ij}^{\,0}(r|v_{ij}^{\,S}) - 1\}\big] - \tilde{g}_{ij}(r)\boldsymbol{\nabla}\beta v_{ij}^{\,L}(r), \quad (2\cdot16)^{*)}$$

where

$$\mathscr{F}_Q\{\tilde{g}_{ij}^{\,0}(r|v_{ij}^{\,S}) - 1\} \equiv \{\mathscr{F}_Q[n_i^{\,0}(r|v_{ij}^{\,S})/n_i - 1]\cdot\mathscr{F}_Q[n_j^{\,0}(r|v_{ji}^{\,S}) - 1]\}^{1/2}, \qquad (2\cdot17)$$

and $(\hat{B}_i \hat{B}_j)^{\alpha}$ with a real number α is an operator defined by

$$\mathscr{F}_Q\big[(\hat{B}_i \hat{B}_j)^{\alpha}f(r)\big] \equiv (\chi_Q^{\,0i}\chi_Q^{\,0j})^{\alpha}\mathscr{F}_Q[f(r)] \qquad (2\cdot18)$$

acting on any function $f(r)$ which has the Fourier transform.

It should be kept in mind that there is the Ornstein-Zernike relation between $\tilde{g}_{ij}(r)$ and $\widetilde{C}_{ij}(r)$ for quantal mixtures which is written in the form

---

*) Eq. (2·57) of I.

$$\widetilde{g}_{ij}(r) - 1 = (B_i B_j)^{1/2} \widetilde{C}_{ij}(r) + \sum_l \int \{ \widetilde{g}_{il}(|\boldsymbol{r} - \boldsymbol{r}'|) - 1 \} n_l (B_i B_j)^{1/2} \widetilde{C}_{lj}(r') d\boldsymbol{r}' .$$

$$(2 \cdot 19)^{*)}$$

In general, the isothermal compressibility κ_T of a binary mixture is given by the formula**)

$$\frac{\beta}{\kappa_T} = \lim_{Q \to 0} \sum_{k,l} n_k n_l \mathscr{F}_Q \left[\frac{\partial \{ -\beta U_k(r) \}}{\partial n_l(r')} \right], \qquad (2 \cdot 20)$$

which can be written with the aid of Eq. $(2 \cdot 1)$ for a quantal mixture in the form

$$\frac{\beta}{\kappa_T} = \lim_{Q \to 0} \left\{ \frac{n_1}{\chi_Q^{01}} + \frac{n_2}{\chi_Q^{02}} - n_1^2 \widetilde{C}_{11}(Q) - n_2^2 \widetilde{C}_{22}(Q) - 2n_1 n_2 \widetilde{C}_{12}(Q) \right\}. \qquad (2 \cdot 21)$$

For a classical neutral binary mixture, Eq. $(2 \cdot 21)$ is reduced to a well-known form[13]

$$\frac{\beta}{\kappa_T} = n_1 + n_2 - n_1^2 C_{11}(0) - n_2^2 C_{22}(0) - 2n_1 n_2 C_{12}(0). \qquad (2 \cdot 22)$$

§ 3. Formulas in liquid metals

(A) *Response and correlation functions*

In liquid metals, we can deal with the ions classically, so that the results of § 2 can be written in simpler forms because of $\chi_Q^{0I} = 1$ and $\chi_Q^{II} = S_{II}(Q)$, and the free-ion polarizability is given by a classical one

$$\chi_Q^{0I}(\omega) = 1 - \frac{x}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{x - t} dt \qquad (3 \cdot 1)$$

with $x \equiv (\omega/Q) \sqrt{M_I \beta/2}$. In liquid metals, the Fermi energy E_F of the electron gas is so high compared with the temperature of liquid metals that the electron gas is treated as at absolute zero temperature. Therefore, the free-electron polarizability in the zero self-energy approximation may be written as

$$\beta \chi_Q^{0e}(\omega) = \frac{2}{3E_F} \left[\frac{1}{2} + \frac{1}{2\overline{Q}} \{ \Phi(y_+) + \Phi(y_-) \} \right], \qquad (3 \cdot 2)$$

$$\Phi(z) \equiv (1 - z^2) \ln \{ (z+1)/(z-1) \} \qquad (3 \cdot 3)$$

with $y_\pm \equiv \overline{Q}/2 \pm (1/2\overline{Q}) \cdot (\overline{\omega} + 0^+)$ in units of the Fermi-wave number Q_F and E_F.

Thus, we can express the density-density canonical correlations in terms of

---

*) Eq. $(2 \cdot 41)$ of I.

**) This equation may be obtained by extending the derivation of Kirkwood-Buff[22] to the case of the relations between Q-dependent quantities with the use of the formula[23]

$$\partial n_i / \partial \beta \mu_j = \lim_{Q \to 0} \mathscr{F}_Q [\delta n_i(r|U) / \delta \{ -\beta U_j(r') \}]$$

$$= \lim_{Q \to 0} \sqrt{n_i n_j} \chi_Q^{ij} .$$

the DCF by taking the Fourier transform of the Ornstein-Zernike relation

$$S_{II}(Q) = \chi_Q^{II} = \{1 - n_e \widetilde{C}_{ee}(Q) \chi_Q^{0e}\} / D(Q), \tag{3.4}$$

$$S_{eI}(Q) = \chi_Q^{eI} = (n_e n_I)^{1/2} \widetilde{C}_{eI}(Q) \chi_Q^{0e} / D(Q), \tag{3.5}$$

$$\chi_Q^{ee} = \{1 - n_I \widetilde{C}_{II}(Q)\} \chi_Q^{0e} / D(Q) \tag{3.6}$$

with

$$D(Q) \equiv \{1 - n_I \widetilde{C}_{II}(Q)\} \{1 - n_e \widetilde{C}_{ee}(Q) \chi_Q^{0e}\} - n_I n_e \widetilde{C}_{Ie}^2(Q) \chi_Q^{0e}. \tag{3.7}$$

At this point, it is important to realize that, although the electrons in a liquid metal behave as a quantum fluid, the density-density canonical correlation of electron-ions χ_Q^{eI} reduces to classical form, namely, the structure factor $S_{eI}(Q)$: the reason for this fact is discussed later.

The relation (2.7) in the case of liquid metals states that, when an ion is fixed at the origin, the electron density distribution around it is connected to $S_{eI}(Q)$ by the relation

$$n_e \mathcal{F}_Q \left\{ \frac{n_e(r|I)}{n_e} - 1 \right\} = \chi_Q^{eI} = S_{eI}(Q), \tag{3.8}$$

which is rewritten by the inverse Fourier transform as

$$n_e(r|I)/n_e = g_{eI}(r) = g_{Ie}(r). \tag{3.9}$$

In the case where an electron is fixed at the origin, the ion density distribution around it satisfies the relation

$$n_I \mathcal{F}_Q \left\{ \frac{n_I(r|e)}{n_I} - 1 \right\} = \frac{\chi_Q^{Ie}}{\chi_Q^{0e}} = \frac{S_{Ie}(Q)}{\chi_Q^{0e}}, \tag{3.10}$$

that is, $n_I(r|e)/n_I \neq g_{Ie}(r)$. In this respect, we should refer to the work by Cowan and Kirkwood,[1] in which they used the relation $n_I(r|e)/n_I = n_e(r|I)/n_e$ in their calculation for $g_{Ie}(r)$ in liquid metals with the aid of the Debye-Hückel, Thomas-Fermi theory. However, this relation is not an exact one as shown by Eqs. (3.8) and (3.10) since the electrons in a liquid metal constitute a quantum fluid. Also, their identification $n_e(r|e)/n_e = g_{ee}(r)$ is no longer exact in a liquid metal.

It is important to know the distinction between $n_i(r|j)/n_i$ and $g_{ij}(r)$ in quantum fluids although $n_i(r|j)/n_i = g_{ij}(r)$ in classical fluids. In previous work[14] on the electron gas in the jellium model, we have calculated the electron density distribution around a fixed electron $n(r|v)/n_e$ and the radial distribution function $g(r)$, and have shown that these two quantities are different from each other for small interparticle separation while they become identical in the large distances: The reason for this difference is attributed to the recoil effect and the indistinguishability of identical particles since $n(r|v)/n_e$ is identical with the density distribution around a point impurity particle with an infinite mass and the same charge as an electron. The same is the situation for the electrons in a liquid metal.

Following March and Tosi[5] we can define an effective direct correlation function of ions as

$$g_{II}(r) - 1 = C_{II}^{\text{eff}}(r) + n_I \int \{g_{II}(r') - 1\} C_{II}^{\text{eff}}(|r - r'|) dr' , \qquad (3 \cdot 11)$$

and treat liquid metals as one-component systems. From the Fourier transform of the Ornstein-Zernike relation (2·19), we can rewrite the definition of $C_{II}^{\text{eff}}(Q)$ as

$$1 - n_I C_{II}^{\text{eff}}(Q) = \frac{1 - n_I \widetilde{C}_{II}(Q)}{1 - n_e \widetilde{C}_{ee}(Q) \chi_Q^{0e}} \cdot \frac{\chi_Q^{0e}}{\chi_Q^{ee}} . \qquad (3 \cdot 12)$$

This expression differs from that of March and Tosi[5] in that χ_Q^{ee} and χ_Q^{0e} are replaced by $S_{ee}(Q)$ and unity, respectively: This distinction comes from the fact that their definition of the DCF is the same as that of the classical DCF of binary mixtures. On the other hand, an effective DCF defined above may be introduced from a different point of view. The ion-ion response function of liquid metals in the two-component model is written on the basis of a generalized Hartree approximation[11] in the form

$$\chi_Q^{II}(\omega) = \frac{\chi_Q^{0I}(\omega)}{1 + n_I \beta v_{II}^{\text{eff}}(Q, \omega) \chi_Q^{0I}(\omega)} , \qquad (3 \cdot 13)$$

where

$$\beta v_{II}^{\text{eff}}(Q, \omega) \equiv -\widetilde{C}_{II}(Q) / \varepsilon_e^*(Q, \omega) , \qquad (3 \cdot 14)$$

$$1/\varepsilon_e^*(Q, \omega) = 1 - \frac{\widetilde{C}_{Ie}^2(Q)}{\widetilde{C}_{II}(Q) \widetilde{C}_{ee}(Q)} \{1 - 1/\varepsilon_I(Q, \omega)\} . \qquad (3 \cdot 15)$$

If we neglect ω-dependence of $v_{II}^{\text{eff}}(Q, \omega)$, Eq. (3·14) reduces exactly to

$$n_I \beta v_{II}^{\text{eff}}(Q, \omega = 0) = 1/S_{II}(Q) - 1 = -n_I C_{II}^{\text{eff}}(Q) , \qquad (3 \cdot 16)$$

that is, in this approximation Eq. (3·13) is written as

$$\chi_Q^{II}(\omega) = \frac{\chi_Q^{0I}(\omega)}{1 - n_I C_{II}^{\text{eff}}(Q) \chi_Q^{0I}(\omega)} . \qquad (3 \cdot 17)$$

This is nothing but the result from a one-component model for liquid metals, where $C_{II}^{\text{eff}}(Q)$ is used to calculate $\chi_Q^{II}(\omega)$. Therefore, introduction of $C_{II}^{\text{eff}}(Q)$ in an attempt to treat liquid metals as one-component systems is equivalent to the neglect of ω-dependence of $v_{II}^{\text{eff}}(Q, \omega)$ in the two-component model in the generalized Hartree approximation. The result of numerical calculation based on Eqs. (3·13) and (3·17) is shown in § 4.

(B) *Compressibility and Friedel sum rule*

Before proceeding to the numerical calculation of correlations, we may discuss the general properties of a liquid metal, provided that we can divide the electrons distinctively into core and conduction electrons as is the case in a simple liquid

metal.

From Eqs. $(3 \cdot 4)$ to $(3 \cdot 6)$, we obtain in the zero wave-number limit

$$\lim_{Q \to 0} \frac{\chi_Q{}^{II}}{\chi_Q{}^{ee}} = \lim_{Q \to 0} \frac{1 - n_e \widetilde{C}_{ee}(Q) \chi_Q{}^{0e}}{\{1 - n_I \widetilde{C}_{II}(Q)\} \chi_Q{}^{0e}} = \frac{1}{Z}, \qquad (3 \cdot 18)$$

and similarly

$$\lim_{Q \to 0} \chi_Q{}^{Ie}/\chi_Q{}^{ee} = 1/\sqrt{Z}, \qquad (3 \cdot 19)$$

since in the small Q region the DCF have the following singularities due to the Coulomb interaction:

$$\widetilde{C}_{ij}(Q) \sim -\beta \frac{4\pi e_i e_j}{Q^2}. \qquad (3 \cdot 20)$$

By combining Eqs. $(3 \cdot 18)$ and $(3 \cdot 19)$, we find

$$\chi_{Q=0}^{ee} = Z \chi_{Q=0}^{II} = \sqrt{Z} \, \chi_{Q=0}^{Ie}, \qquad (3 \cdot 21)$$

which is written in an alternative form:

$$S_{ee}(0) = Z S_{II}(0) = \sqrt{Z} \, S_{Ie}(0), \qquad (3 \cdot 22)$$

because of general relations[23] in binary mixtures

$$\lim_{Q \to 0} (n_i n_j)^{1/2} \chi_Q{}^{ij} = -\frac{\partial n_i}{\partial (\beta \mu_j)} = (n_i n_j)^{1/2} S_{ij}(0). \qquad (3 \cdot 23)$$

These results, $(3 \cdot 21)$ and $(3 \cdot 22)$, have been obtained previously.[4],[8]

Next, we express the structure factors in the zero wave-number limit in terms of the isothermal compressibility of a liquid metal. In the first place, we shall try to write $S_{II}(0)$ in terms of the DCF; Eq. $(3 \cdot 4)$ is rewritten as

$$\frac{1}{\chi_Q{}^{II}} = 1 - \frac{n_I \widetilde{C}_{II}(Q) - n_I \widetilde{C}_{II}(Q) n_e \widetilde{C}_{ee}(Q) \chi_Q{}^{0e} \{1 - \widetilde{C}_{Ie}^2(Q)/\widetilde{C}_{II}(Q) \widetilde{C}_{ee}(Q)\}}{1 - n_e \widetilde{C}_{ee}(Q) \chi_Q{}^{0e}}, \qquad (3 \cdot 24)$$

whence we obtain by taking the zero wave-number limit

$$\lim_{Q \to 0} \frac{1}{\chi_Q{}^{II}} = 1 + \frac{Z}{\chi_{Q=0}^{0e}} - n_I \widetilde{C}_{II}'(0) - Z^2 n_I \widetilde{C}_{ee}'(0) - 2 Z n_I \widetilde{C}_{ie}'(0), \qquad (3 \cdot 25)$$

because of

$$\lim_{Q \to 0} \beta \frac{4\pi (Ze)^2}{Q^2} \left\{ 1 - \frac{\widetilde{C}_{Ie}^2(Q)}{\widetilde{C}_{II}(Q) \widetilde{C}_{ee}(Q)} \right\} = -\widetilde{C}_{II}'(0) - Z^2 \widetilde{C}_{ee}'(0) - 2Z \widetilde{C}_{Ie}'(0). \qquad (3 \cdot 26)$$

In this expression, the prime denotes the non-Coulomb part of the DCF, that is,

$$\widetilde{C}_{ij}'(Q) \equiv \widetilde{C}_{ij}(Q) + \beta \frac{4\pi e_i e_j}{Q^2}. \qquad (3 \cdot 27)$$

In the second place, on making use of Eq. $(2 \cdot 21)$ we can relate $S_{II}(0)$ to the

348   *J. Chihara*

isothermal compressibility as follows:

$$\frac{\beta}{n_I \kappa_T} = 1 + \frac{2}{3} E_F \beta Z - n_I \widetilde{C}'_{II}(0) - Z^2 n_I \widetilde{C}'_{ee}(0) - 2Z n_I \widetilde{C}'_{Ie}(0)$$

$$= 1/S_{II}(0). \tag{3.28}$$

Here, we have used the relation[15] $\lim_{Q \to 0} \beta \chi_Q^{0e} = 2/3 E_F$ which yields to the Bohm-Staver term[16] in the above formula for κ_T.

Now, the above results are summarized as

$$S_{ee}(0) = Z S_{II}(0) = \sqrt{Z} S_{Ie}(0) = Z n_I k_B T \kappa_T, \tag{3.29}$$

where

$$\frac{1}{n_I k_B T \kappa_T} = 1 + \frac{2E_F}{3k_B T} Z - n_I \widetilde{C}'_{II}(0) - Z^2 n_I \widetilde{C}'_{ee}(0) - 2Z n_I \widetilde{C}'_{Ie}(0). \tag{3.30}$$

It is important to realize that if we use the classical form of the DCF, as was done by March and Tosi,[5],[6] the Bohm-Staver term does not appear in the formula for the isothermal compressibility.

Furthermore, we can also obtain the similar formula for fused salts by taking the classical limit of Eq. (3.25) and by putting $Z = 1$ and $n_1 = n_2 = n$

$$\frac{1}{n k_B T \kappa_T} = 2 - n C'_{11}(0) - n C'_{22}(0) - 2n C'_{12}(0), \tag{3.31}$$

and there follows the same relation as that of liquid metals

$$S_{11}(0) = S_{22}(0) = S_{12}(0) = n k_B T \kappa_T. \tag{3.32}$$

A recent experimental result obtained by Page and Mika[17] for molten CuCl indicates the trend to be consistent with the relation (3.32) in the small wave-number region.

Moreover, the physical significance of the relations (3.21) and (3.22) can be clarified by rewriting them in the form

$$-Ze = -e \int \{n_e(r|I) - n_e\} d\mathbf{r} + Ze \int \{n_I(r|I) - n_I\} d\mathbf{r}, \tag{3.33}$$

$$-Ze = -e n_e \int \{g_{eI}(r) - 1\} d\mathbf{r} + Ze n_I \int \{g_{II}(r) - 1\} d\mathbf{r}, \tag{3.34}$$

which mean that the net charge surrounding a given ion is equal to the negative of the charge on itself. By combining Eqs. (3.33) and (3.34) we obtain

$$\int \{n_e(r|I) - n_e\} d\mathbf{r} = n_e \int \{g_{eI}(r) - 1\} d\mathbf{r} = Z S_{II}(0). \tag{3.35}$$

Since the electron density distribution $n_e(r|I)$ around a fixed ion can be represented in terms of phase shifts $\eta_l(Q)$, we obtain from Eq. (3.35) the Friedel sum rule concerning the electron distribution around a constituent ion in a liquid metal

$$\int \{n_e(r|I) - n_e\} \, d\boldsymbol{r} = Z S_{II}(0) = \frac{2}{\pi} \sum_l (2l+1) \eta_l(Q_F). \qquad (3 \cdot 36)$$

This equation shows that the distortion of the electron density around a constituent ion in a liquid metal is small due to the factor $S_{II}(0)$ which is of order 10^{-2}, and also phase shifts $\eta_l(Q_F)$ will be small. This situation presents a strong contrast with the case of an impurity ion in an electron gas immersed in the uniform background of positive charges, where the ion is screened by building up the large electron accumulation around it to fulfil the condition

$$\int \{n_e(r|I) - n_e\} \, d\boldsymbol{r} = Z. \qquad (3 \cdot 37)$$

This fact can be understood more clearly by noting that in Eq. $(3 \cdot 33)$ the second term on the right-hand side makes larger contribution to compensate the positive charge of the ion than the first term; that is, the ion constituting the liquid metal keeps the charge neutrality by displacing away the positive charges (ions) rather than by inducing the electron charge accumulation around it.

In addition, this situation can also be investigated from another point of view. In the hypernetted chain approximation an effective mean field potential experienced by electrons around a given ion is expressed by Eq. $(2 \cdot 13)$, of which the Fourier transform is written as

$$v_{eI}^H(Q) = v_{eI}(Q) + \frac{1}{\beta} \widetilde{C}_{eI}(Q) - \frac{1}{\beta} \frac{\widetilde{C}_{eI}(Q)}{\widetilde{\varepsilon}_{ee}(Q)} \qquad (3 \cdot 38)$$

with $\widetilde{\varepsilon}_{ee}(Q) \equiv 1 - n_e \widetilde{C}_{ee}(Q) \chi_Q^{0e}$. If we take a pseudo-potential approximation to $v_{eI}(r)$, the electron-ion interaction can be treated as a weak one so that it is valid to approximate $\widetilde{C}_{eI}(Q) = -\beta v_{eI}(Q)$, which is nothing but the random-phase approximation; then we obtain

$$v_{eI}^H(Q) \doteq \frac{v_{eI}(Q)}{\widetilde{\varepsilon}_{ee}(Q)} S_{II}(Q), \qquad (3 \cdot 39)$$

and in the zero wave-number limit

$$v_{eI}^H(0) = -\frac{2}{3} E_F Z S_{II}(0). \qquad (3 \cdot 40)$$

Therefore, we realize that the effective electron mean field potential caused by the ion is small in the small wave-number region owing to the factor $S_{II}(0)$.

§ 4. Numerical calculation

In the preceding section, we have studied the general properties of simple liquid metals on the basis of the result of I. In this section we calculate the structure factors $S_{ij}(Q)$, the RDF $g_{ij}(r)$ and the dynamic structure factors $S_{ij}(Q, \omega)$ of a liquid metal with the use of model potentials

$$v_{II}(r) = (Ze)^2 \, \mathrm{erf}(\zeta_1 r)/r - \text{hard-sphere}, \tag{4·1}$$

$$v_{Ie}(r) = -Ze^2 \, \mathrm{erf}(\zeta_2 r)/r, \tag{4·2}$$

$$v_{ee}(r) = e^2/r. \tag{4·3}$$

As integral equations for χ_Q^{ij}, we use Eq. (2·16) with $v_{ee}^S = v_{Ie}^S = 0$, of which the Fourier transforms are written as

$$\widetilde{C}_{II}(Q) = -\beta v_{II}^L(Q)\{1 - G_{II}(Q)\} + \widetilde{C}_{II}^S(Q), \tag{4·4}$$

$$\widetilde{C}_{Ie}(Q) = -\beta v_{Ie}(Q)\{1 - G_{Ie}(Q)\}, \tag{4·5}$$

$$\widetilde{C}_{ee}(Q) = -\beta v_{ee}(Q)\{1 - G_{ee}(Q)\}, \tag{4·6}$$

where

$$n_I \beta v_{II}^L(Q) G_{II}(Q) = -\left(\frac{\hbar\omega_p}{2E_F}\right)^2 \left(\frac{2E_F}{k_B T}\right) Z \frac{3}{8\bar{Q}^3} \int_0^\infty dt\, t\, \{S_{II}(t) - 1\}\, h(\bar{Q}, t; \alpha_{II}), \tag{4·7}$$

$$(n_I n_e)^{1/2} \beta v_{Ie}(Q) G_{Ie}(Q) = \left(\frac{\hbar\omega_p}{2E_F}\right)^2 \left(\frac{2E_F}{k_B T}\right) \sqrt{Z} \frac{3}{8\bar{Q}^3} \int_0^\infty dt\, t\, \tilde{S}_{Ie}(t)\, h(\bar{Q}, t; \alpha_{Ie}), \tag{4·8}$$

$$G_{ee}(Q) = -\frac{3}{4} \int_0^\infty dt\, \{\tilde{S}_{ee}(t) - 1\}\, t^2 \left\{1 - \frac{\bar{Q}^2 - t^2}{2\bar{Q}t} \ln\frac{\bar{Q} + t}{\bar{Q} - t}\right\}, \tag{4·9}$$

$$h(p, t; \alpha) \equiv \int_{|p-t|}^{p+t} d\xi\, \frac{\exp(-\alpha^2 \xi^2)}{\xi}(\xi^2 + p^2 - t^2)$$

$$= \frac{1}{2\alpha}\{e^{-\alpha^2(p-t)^2} - e^{-\alpha^2(p+t)^2}\} + \frac{p^2 - t^2}{2}[E_1\{\alpha^2(p-t)^2\} - E_1\{\alpha^2(p-t)^2\}],$$

$$E_1(x) \equiv \int_x^\infty \frac{\exp(-t)}{t} dt; \quad \tilde{S}_{ij}(Q) \equiv \chi_Q^{ij}/(\chi_Q^{0i}\chi_Q^{0j})^{1/2} \tag{4·10}$$

and

$$n_I C_{II}^S(Q) = F(\bar{Q}) + n_I \int K(\bar{Q}, s)\{\tilde{\gamma}_{II}(s) + \tilde{\gamma}_{Ie}(s) + \widetilde{C}_{II}^L(s)\}\, ds, \tag{4·11}$$

$$F(\bar{Q}) \equiv -24\eta\{\sin(\alpha\bar{Q}) - \alpha\bar{Q}\cos(\alpha\bar{Q})\}/(\alpha\bar{Q})^3, \tag{4·12}$$

$$K(\bar{Q}, s) \equiv \frac{\alpha}{\pi\bar{Q}}\left[\frac{\sin\{(\bar{Q} + s)\alpha\}}{(\bar{Q} + s)\alpha} - \frac{\sin\{(\bar{Q} - s)\alpha\}}{(Q - s)\alpha}\right], \tag{4·13}$$

$$\tilde{\gamma}_{II}(Q) \equiv \{S_{II}(Q) - 1\}\widetilde{C}_{II}(Q); \quad \tilde{\gamma}_{Ie}(Q) \equiv \chi_Q^{Ie}\widetilde{C}_{Ie}(Q) \tag{4·14}$$

with $\bar{Q} = Q/Q_F$, $\alpha = Q_F a_H$, $\omega_p^2 = 4\pi e^2 n_e/m_e$ and η the packing fraction.

In this calculation, the parameters of the model are taken as appropriate to Na in the following way: The diameter of a hard-sphere, $a_H = 3.4$ A, the packing fraction $\eta = \pi n_I a_H^3/6 = 0.45$, the mass ratio of ion to electron $M_I/m_e = 4200$, $Z = 1$, $T = 500°$C, $\zeta_1 Q_F = 0.2$ and $\zeta_2 = \sqrt{2}\,\zeta_1$. These parameters give the factor $\mathrm{erf}(\zeta_1 r)$

to the long-range part of the ion-ion potential the following values: $\mathrm{erf}(\zeta_1 a_{II})=0.6$, $\mathrm{erf}(\zeta_1 \cdot 2a_{II})=0.9$ and $\mathrm{erf}(\zeta_1 \cdot 3a_H)=0.99$.

The equations from $(4 \cdot 4)$ to $(4 \cdot 6)$ are solved by an iterative procedure. In order to avoid the difficulty associated with the Coulomb divergence, we treat the small wave-number region with the use of the relation

$$\widetilde{C}_{II}(Q)\widetilde{C}_{ee}(Q) - \widetilde{C}_{Ie}^2(Q) = \widetilde{C}_{II}(Q)\widetilde{C}_{ee}(Q)A(Q), \qquad (4\cdot15)$$

where

$$A(Q) \equiv \frac{1 - B(Q) + \widetilde{C}_{II}^{\mathrm{S}}(Q)/\widetilde{C}_{II}^{\mathrm{L}}(Q)}{1 + \widetilde{C}_{II}^{\mathrm{S}}(Q)/\widetilde{C}_{II}^{\mathrm{L}}(Q)}, \qquad (4\cdot16)$$

$$B(Q) \equiv \{\widetilde{C}_{Ie}^{\mathrm{L}}(Q)\}^2 / \{\widetilde{C}_{II}^{\mathrm{L}}(Q)\widetilde{C}_{ee}(Q)\}. \qquad (4\cdot17)$$

Once we solved equations for χ_Q^{ij}, we can obtain immediately the ion-ion and electron-ion RDF by their inverse Fourier transforms, since $\chi_Q^{II} = S_{II}(Q)$ and $\chi_Q^{eI} = S_{eI}(Q)$. In order to obtain the electron-electron RDF, however, we must evaluate the following integral:

$$S_{ee}(Q) = \int_{-\infty}^{\infty} \frac{1}{1 - e^{-\beta\omega}} \mathrm{Im}\,\{\beta\chi_Q^{ee}(\omega)\}\,d\omega\,. \qquad (4\cdot18)$$

This integral can be transformed by a suitable choice of contours[18] into the form

$$S_{ee}(Q) = \chi_Q^{ee}(0) + 2\sum_{k=1}^{\infty} \chi_Q^{ee}\left(\frac{2\pi k}{\beta}i\right). \qquad (4\cdot19)$$

By using Eqs. $(2\cdot8)$ and $(2\cdot9)$, the right-hand side of Eq. $(4\cdot19)$ is represented in terms of

$$\chi_Q^{0I}(iw) = 1 - \sqrt{\pi}\,y e^{y^2}\,\mathrm{erfc}(y), \qquad (4\cdot20)$$

$$\beta\chi_Q^{0e}(iw) = \frac{3}{2E_{\mathrm{F}}}\left[\frac{1}{2} + \frac{1-q^2+v^2}{8q}\ln\frac{(1+q)^2+v^2}{(1-q)^2+v^2} - \frac{v}{2}\left\{\tan^{-1}\left(\frac{1-q}{v}\right) + \tan^{-1}\left(\frac{1+q}{v}\right)\right\}\right]$$

$$(4\cdot21)$$

with $y \equiv \sqrt{(E_{\mathrm{F}}/kT_{\mathrm{B}})\cdot(M_I/m_e)}\,(w/2E_{\mathrm{F}})(Q_{\mathrm{F}}/Q)$, $q = Q/2Q_{\mathrm{F}}$ and $v \equiv (W/2E_{\mathrm{F}}) \times (Q/Q_{\mathrm{F}})$. The sum in Eq. $(4\cdot19)$ has been carried out by using Gregory's formula.[19] It should be mentioned, at this point, that $S_{eI}(Q)$ can be approximated by χ_Q^{eI} since $S_{eI}(Q)$ can be, also, expressed exactly by the sum similar to Eq. $(4\cdot19)$ and all terms except $\chi_Q^{eI}(0) = \chi_Q^{eI}$ are very small compared with it.

In Fig. 1 the structure factors $S_{ij}(Q)$ are shown; the dotted curve denotes $S_{II}(Q)$ calculated from the Percus-Yevick hard-sphere model with $\eta = 0.45$. On comparison with the Percus-Yevick result, the main peak position is shifted to the small wave-number side and its shape is distorted asymmetrically. The shoulder in the main peak comes from the ion-ion potential consisting of the hard-sphere part and the Coulomb part. This shoulder is present also in the case of the one-
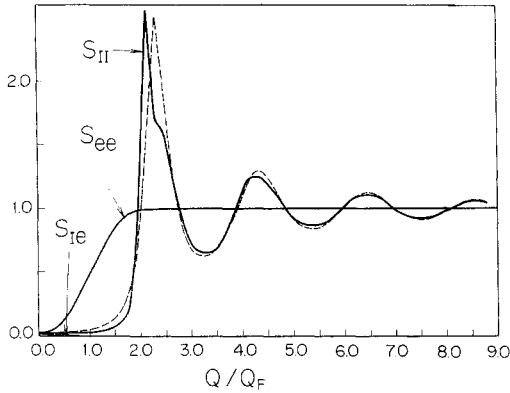
Fig. 1. Structure factors of ions, electron-ions and
electrons. The dotted curve is calculated from the
Percus-Yevick hard-sphere model with $\eta=0.45$.

component model[20] for an ion fluid immersed in the negative charge background, if we use the same ion-ion potential and the same integral equation to this case. The electron-electron structure factor $S_{ee}(Q)$ shows no significant difference except near $Q=0$ in comparison with that calculated from the jellium model.[14] It should be noted that the ion-electron structure factor $S_{Ie}(Q)$ is very small.

In the case where χ_Q^{ij} are determined by Eq. (2·16) the compressibility can be represented as

$$\frac{1}{n_I k_B T \kappa_T} = 1 + \frac{2E_F}{3k_B T} - \frac{2E_F}{3k_B T}(\mu_{II} + \mu_{ee} - 2\mu_{Ie})$$
$$- n_I \widetilde{C}_{II}^S(0) - n_I \widetilde{C}_{ee}^S(0) - 2n_I \widetilde{C}_{Ie}^S(0), \qquad (4\cdot22)$$

where

$$\mu_{ij} \equiv \lim_{Q \to 0} \frac{n_i n_j}{n_I} \beta v_{ij}^L(Q) G_{ij}(Q)$$
$$= \frac{1}{2} \int_0^\infty dt \{\widetilde{S}_{ij}(t) - \delta_{ij}\} t \left[\frac{d}{dt}\{t^2 \phi_{ij}(t)\} + t\phi_{ij}(t) \right], \qquad (4\cdot23)$$

$$\phi_{ij}(Q/Q_F) \equiv \frac{3\pi}{8\alpha r_s Z} \frac{n_i n_j}{n_I} \frac{v_{ij}^L(Q)}{E_F}. \qquad (4\cdot24)$$

The model potentials (4·1)∼(4·3) and the parameters used in this calculation give the second Bohm-Staver term a values 28.5, the third term 38.0 and the fourth term a value −66.0 with $\widetilde{C}_{ee}^S(0) = \widetilde{C}_{Ie}^S(0) = 0$; the sum of these terms is 58.2. In the third term, μ_{II} and μ_{Ie} are negligible compared with the electron contribution μ_{ee}. This result shows that the hard-sphere part of ion-ion potential has an important contribution to the compressibility in liquid metals as well as the Bohm-Staver term and electron correlation.

The RDF $g_{ij}(r)$ are shown in Fig. 2. At first sight it is surprising that there is no effective correlation between ion and electron in this model. As is well known in the Wigner-Seitz method for the calculation of band structures, an ion in a simple solid metal does not disturb the uniform electron density distribution significantly except in the ion core region. The above result $g_{eI}(r) = 1$ shows that this situation also holds in liquid metals. The analysis in §3 also supports this fact. Therefore, we may expect that in simple liquid metals the ions are
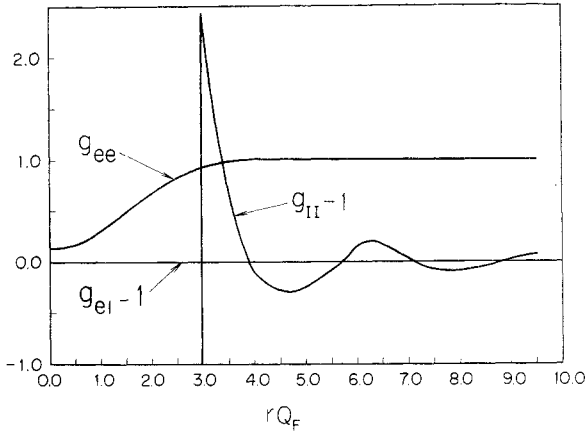
Fig. 2.   Radial distribution functions of ions, electron-
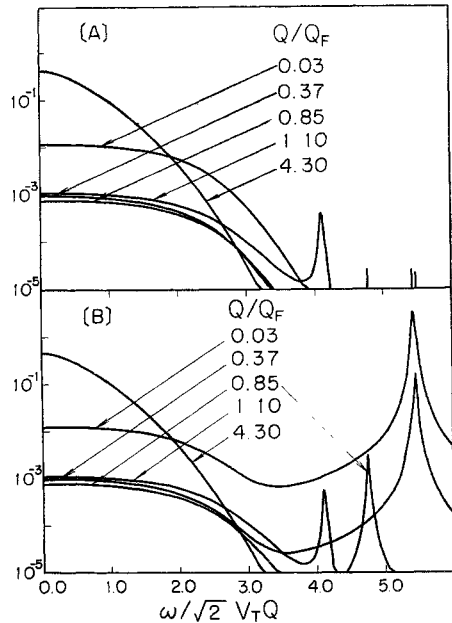ions and electrons.

Fig. 3.   The dynamic structure factor $S_{II}(Q, \omega)$ of ions, calculated from the
one-component model (A) and that from the two-component model (B).
$S_{II}(Q, \omega)$ in (A) has δ-function-like peaks in the positions corresponding
to peaks in (B)

moving around in the homogeneous electron gas as though they had no interaction
with the electrons, and thus the electron gas in the simple liquid metal is quite
consistent with the jellium model; $g_{ee}(r)$ in Fig. 2 coincides with that calculated
from the jellium model.[14]

Curves of the dynamic structure factor of ions $S_{II}(Q, \omega)$ calculated from Eq.
(3·13) are shown in Fig. 3(B): curves in Fig. 3(A) are obtained on the basis of
the one-component model (3·17).   The dynamic structure factor $S_{II}(Q, \omega)$ based
on the two-component model differs from that based on the one-component model
in that the former (Fig. 3(B)) has the broader zero sound peaks than the latter
(Fig. 3(A)) at the small wave-numbers.   This difference is ascribed to the fact
that the zero sound of ions in the two-component model subjects to the Landau
damping due to individual motions of the electrons contrary to the one-component
model.

§ 5.   Concluding remarks

In the present work, we have shown a method of calculating the ionic and
electronic correlations in liquid metals as coupled electron-ion systems.   Since in
a liquid metal the ions behave as a classical fluid and the electrons constitute a
quantum fluid, theories to treat classical and quantum liquids in a unified manner

may be regarded as examined by applying them to liquid metals. In fact, the application of our theory to liquid metals reveals the importance of quantal DCF $\widetilde{C}_{ij}(r)$ in dealing with classical and quantum fluids in a unified fashion:

For example, the compressibility formula (2·21) for a quantal binary mixture is applicable to fused salts, liquid metals as well as classical neutral mixtures; the Bohm-Staver term in formula (3·30) for liquid metals could not be included without the use of the quantal DCF.

Without using the quantal DCF we may not construct also those integral equations for quantum mixtures which reduce to equations for classical mixtures in the limit $\hbar \to 0$; as a simple example, the random-phase approximated equation for quantum mixtures is given by $\widetilde{C}_{ij}(r) = -\beta v_{ij}(r)$, and not by $C_{ij}(r) = -\beta v_{ij}(r)$. In § 4 we have used an integral equation for the ions

$$\nabla \widetilde{C}_{II}(r) = -\nabla \left[g_{II}(r) \left\{ e^{\beta v_{II}^{S}(r)} - 1 \right\} \right] - g_{II}(r) \nabla \beta v_{II}^{L}(r). \qquad (5\cdot1)$$

This equation is quite similar to that used previously for an ion liquid in the uniform negative charge background, except that the DCF is the quantal one: we must use this quantal form in liquid metals due to the presence of electrons which behave as a quantum fluid.

Furthermore, the difference between our definition and that of March-Tosi[5] concerning the effective ion-ion DCF also shows the significance of the quantal DCF: this problem is closely concerned with establishing integral equations with the use of the quantal DCF as mentioned before.

It should be noted that an ion constituting a liquid metal distorts the electron charge distribution so as to satisfy the sum rule $\int \{n_e(r|I) - n_e\} dr = ZS_{II}(0)$, which presents a contrast with the case of an impurity ion in the jellium model: $\int \{n_e \times (r|I) - n_e\} dr = Z$. That is, a constituent ion in the liquid metal displaces only about one-hundredth electrons from the uniform electron distribution compared with an impurity ion in the jellium model due to the factor $S_{II}(0) \sim 10^{-2}$. This fact gives an answer to the difference in the positron annihilation experiments between solids and liquids: a positron in a solid metal cannot push away ions surrounding it so that it behaves as if in the jellium model and satisfies the sum rule (3·37) with $Z=1$ by accumulating electrons around it. On the other hand, a positron in the liquid metal can displace ions off from its surrounding and as a consequence electrons accumulate around it in a much smaller amount than in the solid metal.

In the present calculation we have used model potentials for ion-ion and ion-electron interactions. In order to compare with experimental results of $S_{II}(Q)$, we must use more realistic potentials. In particular, the quantal hypernetted chain equation should be used in attempting to investigate the conduction electron distribution in the core region of an ion, since in this approximation $n_e(r|I)$ can be given by solving the wave equation (2·15). However, RDF, $g_{ee}(r)$ and $g_{Ie}(r)$, in this calculation may not be altered essentially even if we proceed to the calculation in a refined manner as mentioned above, provided that $\int_{\text{core}} \{n_e(r|I) - n_e\} dr \fallingdotseq 0$

as is the case in simple metals.

In simple liquid metals the behaviour of the electron is quite similar to that in the jellium model and the ions are moving through the electron gas without disturbing its uniform charge distribution on the average. This picture makes a strong contrast with Ziman's neutral pseudo-atom model[21] of liquid metals, which states that each ion moves about in a liquid taking with it screening charges rigidly: His model is founded on the linear response theory to calculate the screening charge distribution around each ion.

Acknowledgements

References

1) R. D. Cowan and J. K. Kirkwood, J. Chem. Phys. **29** (1958), 264.
2) Y. Nakahara, J. Nucl. Sci. Tech. **8** (1971), 1.
3) H. Takahashi, Physica **51** (1971), 333.
4) M. Watabe and M. Hasegawa, *Proceedings of the Second International Conference on Liquid Metals* (Taylor and Francis, 1973), p. 133.
5) N. H. March and M. P. Tosi, Ann. of Phys. **81** (1973), 414.
6) M. P. Tosi and N. H. March, Nuovo Cim. **15** (1973), 308.
7) M. P. Tosi, M. Parrinello and N. H. March, Nuovo Cim. **23** (1974), 135.
8) J. Chihara, *Proceedings of the Second International Conference on Liquid Metals* (Taylor and Francis, 1973), p. 137.
9) J. Chihara, Prog. Theor. Phys. **50** (1973), 794.
10) P. A. Egelstaff, N. H. March and N. C. McGill, Can. J. Phys. **52** (1974), 1651.
11) J. Chihara, Prog. Theor. Phys. **47** (1972), 395.
12) J. K. Percus, *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, 1964), II-33.
13) N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156** (1967), 685.
14) J. Chihara, Prog. Theor. Phys. **53** (1975), 400.
15) J. Chihara, Prog. Theor. Phys. **50** (1973), 1156.
16) D. Bohm and T. Staver, Phys. Rev. **84** (1951), 836.
17) D. I. Page and K. Mika, J. Phys. **C4** (1971), 3034.
18) D. Pines, *Elementary Excitations in Solids* (Benjamin, 1963), p. 293.
19) R. A. Buckingham, *Numerical Methods* (Sir Isaac Pitman and Sons, 1957), p. 130.
20) J. Chihara, Prog. Theor. Phys. **50** (1973), 409.
21) J. M. Ziman, Adv. in Phys. **13** (1964), 80.
22) J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **19** (1951), 774.
23) R. Kubo, Reports Prog. Phys. XIX Part 1 (1966), 279.