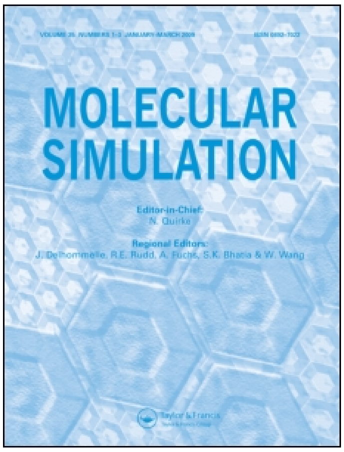

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Effective Interatomic Interactions in Liquid Metals

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EFFECTIVE INTERATOMIC INTERACTIONS IN LIQUID METALS

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Some liquid metals can be regarded as a binary mixture of ions and electrons interacting via binary interparticle interactions with each other. It is shown exactly on the basis of the density-functional method that a liquid metal can be taken as a quasi one-component system only via a pairwise interatomic interaction (without a many-body force) to obtain the radial distribution function, provided that a liquid metal can be thought of as an ion-electron mixture with binary interactions.

KEY WORDS: Effective interaction, liquid metal, density-functional theory, lithium, sodium, radial distribution functions

1 INTRODUCTION

It is not obvious that a liquid metal can be always regarded as a binary mixture of electrons and ions, since we have no clear definition of an "ion", which is applicable to any system. In reality, transition metals, for example, have strongly localized orbitals belonging to continuum states (d-electrons) and their "ionic cores" overlap each other significantly, so that it is not so clear how to define an "ion" for this system. In such a system, many-body forces are obviously important when we treat it as a one-component classical fluid interacting via an effective interatomic interaction.

However, we consider here such a liquid metal where the free electrons are so clearly distinct from the bound electrons forming an "ion", that it can be regarded as a binary mixture of ions and electrons interacting via pair potentials $v_{ij}(r)$. In addition, we assume that the ions behave as classical particles in the sense that the coordinate and momentum of a particle are commutable with each other, while the electrons form quantum fluids. We refer to this system as the ion-electron model hereafter. A simple metal such as a liquid Na is a typical example of the ion-electron model. To this system, the usual pseudopotential method can be applied with considerable success to produce a binary interatomic interaction as a one-component system in the description of it on the basis of the second-order perturbation.

However, in the execution of the molecular-dynamics simulation even on simple liquids, there remains a question whether a liquid metal can be described only in terms of a *binary* interatomic potential. In fact, we cannot neglect the three-body or four-body interatomic interactions which appear from the higher order of the perturbation, if we use a pseudopotential $w_b(r)$ as an ion-electron interaction in the mixture. In the present note, we have shown on the basis of the density-functional theory (DFT) that a liquid metal describable by the ion-electron model can be treated *exactly* as a one-component fluid interacting *only* via a *pairwise* interaction in the determination of the ion-ion radial distribution function.

2 THE ION-ELECTRON MODEL AND THE EFFECTIVE POTENTIAL

If the ion-electron mixture has only *binary* interactions $v_{ij}(r)$ between its constituent particles, the radial distribution functions (RDF) $g_{iI}(r)$ concerning ion are shown to be identical with the inhomogeneous density distributions $n_i(r|I)$ around a fixed ion in the mixture, that is equal to the density distributions $n_i(r|\{U_\alpha = v_{\alpha I}\})$ $[i = I$ or $e]$ under external potentials, $\{U_\alpha(r) = v_{\alpha I}(r)\}$, caused by the ion fixed at the origin:

$$g_{II}(r) = n_I(r|I)/n_0^I = n_I(r|\{U_\alpha = v_{\alpha I}\})/n_0^I \tag{1}$$

$$g_{eI}(r) = n_e(r|I)/n_0^e = n_e(r|\{U_\alpha = v_{\alpha I}\})/n_0^e \tag{2}$$

with uniform densities, n_0^I and n_0^e [1]. The DFT can give *exactly* the inhomogeneous density distributions $n_i(r|U_I, U_e)$ caused by external potentials $\{U_\alpha(r)\}$ in terms of density distributions $n_i^0(r|U_i^{\text{eff}})$ of noninteracting systems under such effective potentials U_i^{eff} as to yield $n_i^0(r|U_i^{\text{eff}}) \equiv n_i(r|U_I U_e)$. This effective interactions are explicitly written as $U_i^{\text{eff}}(r) = U_i(r) + \delta\mathscr{F}_{\text{int}}/\delta n_i(r) - \mu_i^{\text{int}}$ with the interaction part of the intrinsic free-energy $\mathscr{F}_{\text{int}}$ and $\mu_i^{\text{int}} \equiv \mu_i - \mu_i^0$. Here, μ_i and μ_i^0 are chemical potentials of interacting and noninteracting systems of i-kind particles, respectively. In this way, the DF theory can reduce exactly a *many*-body problem to determine the density distribution $n_i(r|U_I U_e)$ of the interacting mixture in the presence of the external potential $\{U_I, U_e\}$ to a *one*-body problem to calculate the density distribution $n_i^0(\mathbf{r}|U_i^{\text{eff}})$ in the noninteracting particles under the effective external potential $U_i^{\text{eff}}(r)$. As a result, the DF theory provides *exact*, although formal, expressions for the RDF's $g_{iI}(r)$ concerning ion as follows [2]

$$g_{iI}(r) = n_i^0(r|U_i^{\text{eff}})/n_0^i \tag{3}$$

$$U_i^{\text{eff}}(r) \equiv v_{iI}(r) - \frac{1}{\beta}\sum_l \int C_{il}(|\mathbf{r} - \mathbf{r}'|)\, n_0^l [g_{lI}(r') - 1]\, d\mathbf{r}' - B_{iI}(r)/\beta \tag{4}$$

in terms of DCF's and bridge functions $B_{iI}(r)$. In the above expression, the DCF's $C_{ij}(r)$ in the ion-electron mixture are defined within the framework of the DF theory by

$$C_{ij}(|\mathbf{r} - \mathbf{r}'|) \equiv -\beta \left.\frac{\delta^2 \mathscr{F}_{\text{int}}[n_I, n_e]}{\delta n_i(\mathbf{r})\delta n_j(\mathbf{r}')}\right|_0, \tag{5}$$

where the suffix 0 denotes the functional derivative at the uniform densities [3].

Actually the explicit expression for the DCF's are given by the Fourier transform of (5) in the matrix form

$$\sqrt{\mathcal{N}}C(k)\sqrt{\mathcal{N}} = (\tilde{\chi}_Q^0)^{-1} - (\tilde{\chi}_Q)^{-1} \tag{6}$$

using the density response functions, $\tilde{\chi}_Q \equiv \|\chi_{ij}(k)\|$ and $\tilde{\chi}_Q^0 \equiv \|\chi^{0i}(Q)\delta_{ij}\|$, of the interacting and noninteracting systems, respectively, with $\mathcal{N} \equiv \|n_0^i\delta_{ij}\|$.

Note here that the density-density response functions $\chi_{iI}(Q)$ concerning ion become identical with structure factors $S_{iI}(Q)$ and $\chi^{0I}(Q) = 1$, if the ions behave as classical particles. Therefore, the structure factors concerning ion in the ion-electron mixture can be described in terms of the DCF's $C_{ij}(Q)$ from (6)

$$S_{II}(Q) = [1 - n_0^e C_{ee}(Q)\chi_Q^0]/D(Q) \tag{7}$$

$$S_{eI}(Q) = \sqrt{n_0^I n_0^e}\, C_{eI}(Q)\chi_Q^0/D(Q) \tag{8}$$

$$= \frac{\rho(Q)}{\sqrt{Z_I}}\, S_{II}(Q), \tag{9}$$

where

$$\rho(Q) \equiv \frac{n_0^e C_{eI}(Q)\chi_Q^0}{1 - n_0^e C_{ee}(Q)\chi_Q^0} \tag{10}$$

$$D(Q) \equiv [1 - n_0^I C_{II}(Q)]\,[1 - n_0^e C_{ee}(Q)\chi_Q^0] - n_0^I n_0^e |C_{eI}(Q)|^2\chi_Q^0 \tag{11}$$

with $\chi_Q^0 = \chi^{0e}(Q)$. At this point, it should be noted that the inverse Fourier transform of (9) leads to the relation:

$$n_0^e g_{eI}(r) = \rho(r) + n_0^I \int \rho(|\mathbf{r} - \mathbf{r}'|)\, g_{II}(r')\mathbf{r}', \tag{12}$$

which states that the condition-electron distribution $n_0^e g_{eI}(r)$ around the fixed ion in the ion-electron mixture can be described exactly by the superposition of surrounding "neutral pseudoatoms", each of which carries about a screening cloud $\rho(r)$. Also, the Ornstein-Zernike (OZ) relations in the ion-electron mixture are obtained from (7) and (8) in the forms

$$g_{II}(r) - 1 = C_{II}(r) + \Gamma_{II}(r) \tag{13}$$

$$g_{eI}(r) - 1 = \hat{B}C_{eI}(r) + \hat{B}\Gamma_{eI}(r) \tag{14}$$

with

$$\Gamma_{ij}(r) \equiv \sum_l \int C_{il}(|\mathbf{r} - \mathbf{r}'|)\, n_0^l\, [g_{lj}(r') - 1]\, d\mathbf{r}', \tag{15}$$

where $\hat{B}$ denotes an operator defined by $\mathscr{F}_{\mathbf{Q}}[\hat{B}^\alpha f(r)] \equiv (\chi_Q^0)^\alpha \int e^{i\mathbf{Q}\cdot\mathbf{r}} f(r)\, d\mathbf{r}$ for an arbitrary real number α. Finally, the RDF's are written to be coupled with (13) and (14) as

$$g_{II}(r) = \exp[-\beta v_{II}(r) + \Gamma_{II}(r) + B_{II}(r)] \tag{16}$$

$$g_{eI}(r) = n_e^0(r|v_{eI} - \Gamma_{eI}/\beta - B_{eI}/\beta)/n_0^e, \tag{17}$$

where $n_e^0(r|U)$ is determined by solving the wave equation for an electron under the external potential $U(r)$.

In the usual approach, a liquid metal is treated as a quasi-one-component fluid interacting via an effective interaction $v^{\text{eff}}(r)$ between ions. For this purpose the effective interaction $v^{\text{eff}}(r)$ can be defined in such a way that the RDF $g(r)$ of the one-component system modelled as a liquid metal should be identical to $g_{II}(r)$ given by (16):

$$g(r) = \exp[-\beta v^{\text{eff}}(r) + \gamma(r) + B(r)] \equiv g_{II}(r) \tag{18}$$

with

$$\gamma(r) \equiv \int C(|\mathbf{r} - \mathbf{r}'|) n_0^I [g(r') - 1] d\mathbf{r}'. \tag{19}$$

Because of the definition: $n_0^I C(Q) \equiv 1 - 1/S_{II}(Q)$, the one-component DCF is related to the ion-ion DCF of the mixture as

$$C(Q) = C_{II}(Q) + \frac{|C_{eI}(Q)|^2 n_0^e \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0}. \tag{20}$$

With the help of (20), it is shown from the definition (18) that the effective potential $v^{\text{eff}}(Q)$ can be expressed exactly as:

$$\beta v^{\text{eff}}(Q) \equiv \beta v_{II}(Q) - \frac{|C_{eI}(Q)|^2 n_0^e \chi_Q^0}{1 - n_0^e C_{ee}(Q) \chi_Q^0}, \tag{21}$$

when the bridge function $B(r)$ of one-component system is taken to be $B_{II}(r)$ of the mixture.

In the above, all equations (1)-(21) are formal, but *exact* expressions within the framework of the DFT. These expressions lead to give an important fact that a liquid metal can be *exactly* described as a one-component fluid interacting only via *pairwise* interaction without introducing many-body potential in the determination of the RDF $g_{II}(r)$, if the ion-ion interaction $v_{II}(r)$ and the electron-ion interaction $v_{eI}(r)$ in the ion-electron model are binary. Furthermore, this effective pairwise interaction can be obtained by a *local* pseudopotential $-C_{eI}(Q)/\beta$ from (21). Also, these exact expressions give a foundation to describe a liquid metal as a pairwise-interacting particles as will be shown bellow.

The integral equations for $g_{II}(r)$ and $g_{eI}(r)$, (16) and (17) coupled with (13) and (14), are rewritten as the equation for the DCF's:

$$C_{II}(r) = \exp[-\beta v_{II}(r) + \Gamma_{II}(r) + B_{II}(r)] - 1 - \Gamma_{II}(r), \tag{22}$$

$$\hat{B} C_{\text{eI}}(r) = n_{\text{e}}^{0f}(r|\tilde{v}_{\text{eI}} - \Gamma_{\text{eI}}/\beta - B_{\text{eI}}/\beta)/n_0^{\text{e}} - 1 - \hat{B}\Gamma_{\text{eI}}(r). \tag{23}$$

A set of integral equations, (22) and (23) with (15), for the DCF's $C_{ij}(r)$ do not form a closed set themselves yet. In order to make closed equations, we introduce some assumptions as follows.

(a) The electron-electron DCF $C_{\text{ee}}(Q)$ is approximated using LFC $G^{\text{jell}}(Q)$ of a jellium model: $C(Q) = -\beta v_{ee}(Q)(1 - G^{\text{jell}}(Q))$.

(b) The ion-ion bridge function $B_{II}(r)$ in (22) is approximated by $B_{\text{PY}}(r; \eta)$ of the Percus-Yevick equation for hard spheres with diameter σ: $B_{II}(r) \simeq$

$B_{PY}(r;\eta)$ with a packing fraction parameter defined by $\eta \equiv \pi n_0^I \sigma^3/6$.

(c) The electron-ion bridge function $B_{eI}(r)$ is neglected: $B_{eI}(r) = 0$.

(d) The ion-ion bare potential $v_{II}(r)$ is taken as coulombic: $v_{II}(r) = (Z_I e)^2/r$.

(e) The bare electron-ion potential $\tilde{v}_{eI}(r)$ is derived as

$$\tilde{v}_{eI}(r) = -Z_A e^2/r + \int v_{ee}(|\mathbf{r}-\mathbf{r}'|)n_e^b(r')d\mathbf{r}' + \mu_{XC}(n_e^b(r) + n_0^e) - \mu_{XC}(n_0^e). \tag{24}$$

by regarding a liquid metal with the atomic number Z_A as a mixture of nuclei and electrons [3]. Here $n_e^b(r)$ denotes the bound-electron distribution, and $\mu_{XC}(n)$ is the exchange-correlation potential. Under these assumptions, equations (22) and (23) generate a closed set of the integral equations for the DCF's $C_{ij}(r)$ (referred to as the QHNC equations). It should be noticed that the QHNC equations can calculate the ionic and electronic structures of a liquid metal from the atomic number Z_A as the only input.

Already, the QHNC integral equations have been successfully applied to many simple metals: lithium [5], sodium [6], potassium and aluminium. Here, we represent the results for lithium and sodium as examples. The structures factor of a liquid lithium at 470 K is shown in Figure 1; the packing fraction η in the bridge function is determined by the use of the RHNC equations giving $\eta = 0.491$ [7]. The QHNC result shows an excellent agreement with the structure factor observed from the neutron-scattering experiment [8]. Another example is a liquid sodium at 373 K,

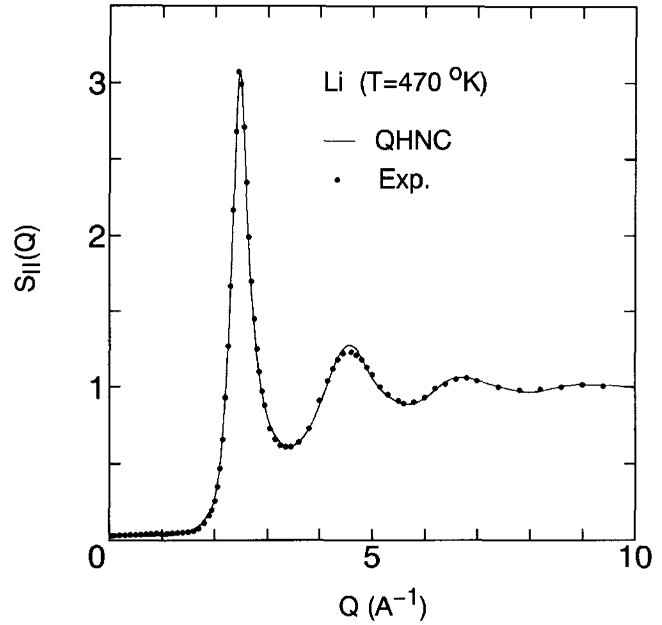

Figure 1 Ion-ion structure factors for Li at 470 K. The QHNC $S_{II}(Q)$ with η determined the RHNC formulatin is compared with that observed by neutron diffraction (solid circles).

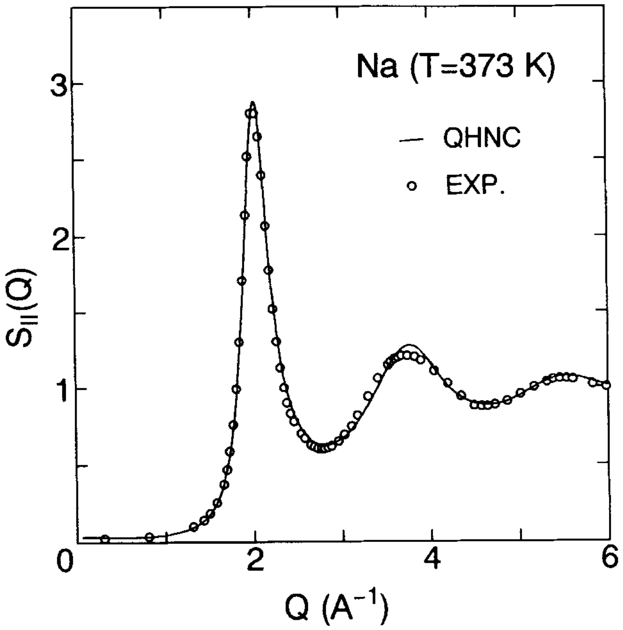

Figure 2 The ion-ion structure factor for Na at 373 K with use of η determined the VMHNC formulation is compared with the experiment (while circles).

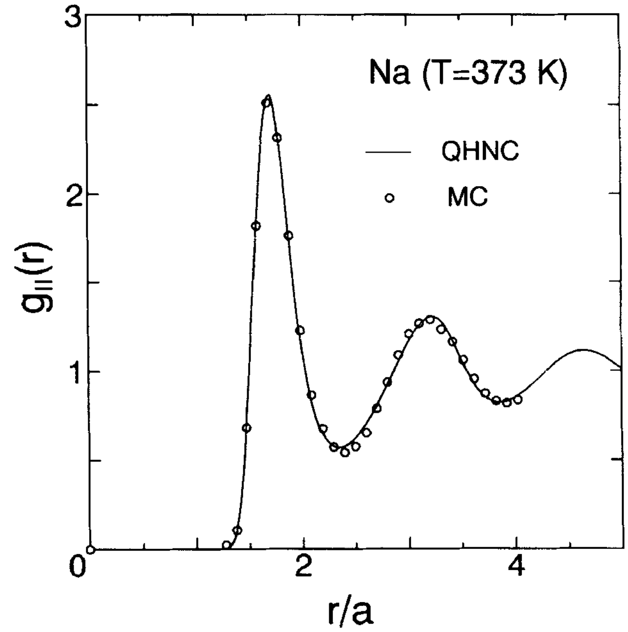

Figure 3 The QHNC radial distribution function (full curve) in comparison with the Monte Carlo result (white circles).

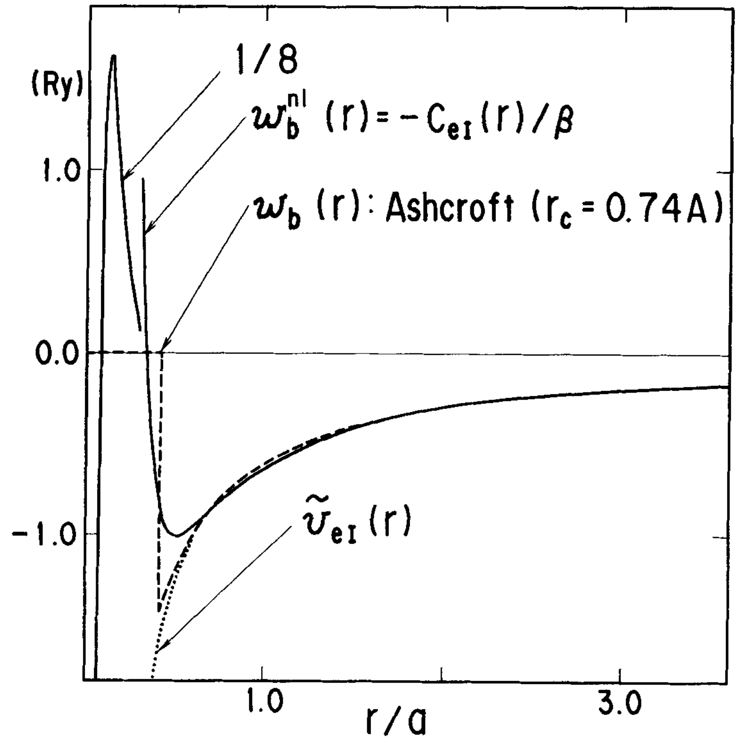

Figure 4 Electron-ion direct correlation function, which plays the role of the pseudopotential, in comparison with the Ashcroft-model potential (dashed curve). Near the origin, it is shown in the reduced scale 1/8.

where the variational MHNC equation [9] is used to determined the packing fraction, although the RHNC equation yields quite same result. In Figure 2, the QHNC structure factor is compared with the experiment [10], while the ion-ion RDF is shown in Figure 3 in comparison with the Monte Calro calculation [11]. In this case, also, the agreement between the QHNC result and the experiment is excellent. In Figure 4, a pseudopotential $-C_{eI}(r)/\beta$ of a liquid lithium is plotted along with the Aschcroft model potential: the electron-ion DCF playing a role of a pseudopotential remains to have an inner-core structure which is smoothed out in the usual pseudopotential in the pseudizing procedure. Due to retaining this inner structure, in spite of taking the form of a linear response formula (10), this pseudopotential can reproduce an inner-core density distribution in a pseudoatom as shown in Figure 5, where the density distribution $\rho(r)$ of a pseudoatom in a liquid sodium is compared with the 3s-electron density distribution $\rho_{3s}(r)$ of a free Na atom.

3 DISCUSSION

The ion-electron model can be applied to a liquid metal where the core-overlapping is negligible and the conduction electrons are clearly distinct from the bound

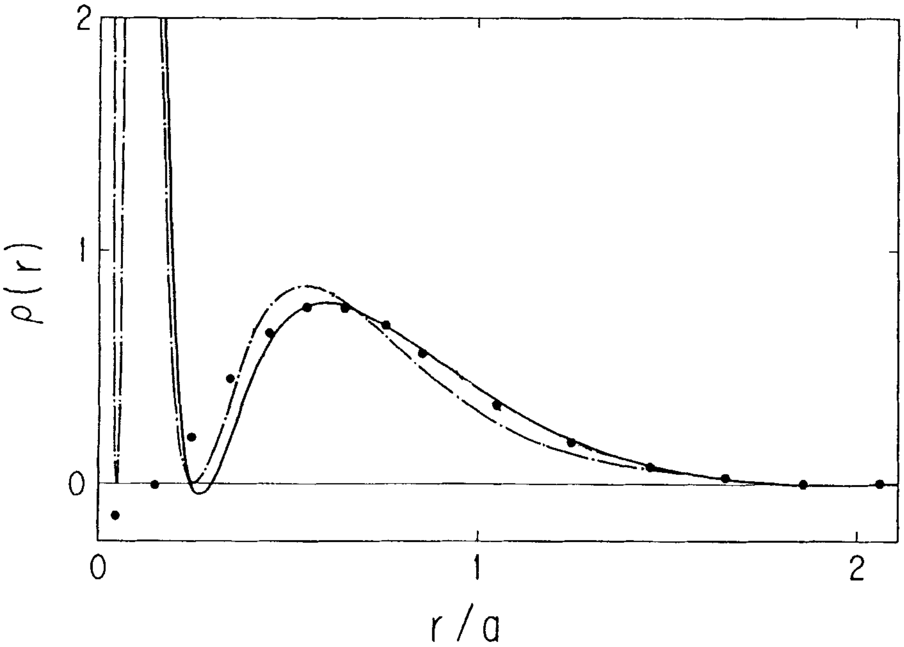

Figure 5 Charge distributions $\rho(r)$ of a neutral pseudoatom in a liquid sodium, calculated by the QHNC method (solid curve) and the pseudopotential method (solid circles), in comparison with the 3s-bound-electron density (chained curve) in a free atom.

electrons forming an ion. In this case, we can applied the ion-electron model, for example, even to a liquid silicon, since its bare ion-ion and electron-ion interactions are regarded as being binary, in spite of the fact that a bonding effect is so strong that many-body interactions are usually thought to be essential in the ion-electron mixture. So it is important that an ion-electron mixture can be exactly described as a one-component liquid with a *pairwise* interaction in the evaluation of the ion-ion RDF even in the case of a liquid silicon which shows bonding properties. In fact, Car and Parrinello (CP) performed molecular-dynamics simulation of a liquid silicon as an ion-electron mixture with the coupled use of the DF theory applied to the electrons in *many-centres* so as to take account of many-body interactions. The CP method is powerful, but time-consuming method.

In the QHNC approach, the pseudopotential $w_b(r) \equiv -C_{el}(r)/\beta$ is evaluated by the equation:

$$\hat{B}C_{\text{el}}(r) = n_e^0(r|\tilde{v}_{\text{el}} - \Gamma_{\text{el}}/\beta)/n_0^e - 1 - \hat{B}\Gamma_{\text{el}}(r), \tag{25}$$

which determines the effective interaction $v^{\text{eff}}(r)$ for the one-component fluid through (21) if the RDF $g_{II}(r)$ is provided. On the other hand the RDF $g_{\text{II}}(r)$ is obtained from the integral equation for the DCF $C(r)$ in the one-component fluid interacting via $v^{\text{eff}}(r)$ evaluated by (21).

$$C(r) = \exp[-\beta v^{\text{eff}}(r) + \gamma(r) + B_{\text{II}}(r)] - 1 - \gamma(r). \tag{26}$$

In this formulation, the effective interatomic interaction $v^{\text{eff}}(r)$ is dependent on the RDF to be determined, since the pseudopotential is dependent on it as (25) states. This formulation suggests that we can perform *ab initio* molecular dynamics using a *pairwise* interaction determined from (21) in order to obtain the ion-ion RDF, which is used again as input to (21) evaluating a new pseudopotential; this process should be repeated to arrive at a convergence. In simple metals, the effective interaction does not dependent significantly on the RDF; it is ascertained that the approximation to the RDF by the step function yields a good effective potential. In this approach, the exchange-correlation effect between conduction electrons is treated by the local-field correction $G^{\text{jell}}(Q)$ of the jellium model as was given by the exact relations in the ion-electron model, while it is represented by the local-density approximation in the CP method.

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