

Ion - ion and electron - ion correlations in liquid gallium

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 4017

(<http://iopscience.iop.org/0953-8984/9/20/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:41

Please note that [terms and conditions apply](#).

Ion–ion and electron–ion correlations in liquid gallium

M Boulahbak, J-F Wax, N Jakse and J-L Bretonnet

Institut de Physique, Université de Metz 1, Boulevard Arago 57078, Metz Cédex 3, France

Received 9 December 1996

Abstract. The ionic and electron–ion structures of liquid Ga are investigated. The ionic pair potential is calculated using Shaw’s optimized model potential and three different local-field corrections: Vashishta and Singwi’s, Ichimaru and Utsumi’s, and the very recent Ortiz and Ballone one. This latter, unlike both of the others, gives pair potentials that predict very well the experimental structure factor of liquid Ga. Investigation of the electron–ion structure factor and the pair distribution function shows an anomalous behaviour that is discussed.

1. Introduction

Liquid Ga exhibits a particular structure factor with a shoulder on the right-hand side of the first peak. It is now clear that this feature is not due to inaccuracy in the experimental results, since the data obtained by many investigators show only small differences (see Bellissent-Funel *et al* (1989) and references 1 to 5 therein). This specificity has to be linked with some other of its physical properties: its low temperature of fusion, its pronounced tendency towards undercooling, the increase of its density on melting by about 3%, the fact that it can solidify in at least four crystalline metastable phases, and so on. Besides this, the shoulder moves to a subsidiary peak during the undercooling (Bizid *et al* 1974).

Many attempts to reproduce these structural anomalies using effective pair potentials constructed on the basis of model potentials have been reported. Fairly good results are obtained with empirical model potentials possessing adjustable parameters (Regnaut *et al* 1980, Mon *et al* 1979), but the results remain disappointing when non-local model potentials free of fitted parameters are used (Bretonnet and Regnaut 1985). In liquid metals, the effective pair potential is notoriously sensitive to the choice of the model potential as well as of the screening function including the exchange–correlation corrections, and a glance at various papers indicates that the potential can differ by an order of magnitude in the region of its first minimum. Hafner and Jank (1990) pointed out that the use of an oversimplified form for the potential such as Ashcroft’s raises difficulties for metals like Ga. Let us recall that, at the scale of the atom, Ga is a trivalent metal with the s^2p^1 valence shell configuration and ten d electrons in the outer shell of the ion, leading to non-negligible core-polarization effects (Mon *et al* 1979). Consequently, the interaction of a valence electron with a Ga core should be complex, and the potential used to describe it is required to be very realistic. Moreover, when dealing with Ga, Bretonnet and Regnaut (1985) noticed the crucial importance of the choice of the dielectric function.

In this paper, we present our results on the structure obtained for Ga when considering the non-local optimized model potential (Shaw 1968) (OMP), free of adjustable parameters, and a new local-field correction. Although not too recent, the OMP can still be considered

the most realistic *ab initio* representation available for simple liquid metals, since it is constructed to reproduce the spectral lines of the free ion. In addition, the exchange–correlation correction used here seems to possess the supplementary features necessary for predicting the structural anomalies of Ga. This local-field function is based on recent Monte Carlo calculations made by Ortiz and Ballone (1994) (OB), who used large systems and took into account the partial spin polarization of the electrons.

The ionic structure factor is calculated using an integral equation based on the soft-core mean-spherical approximation (SMSA) (Madden and Rice 1980) that has successfully described the structure factor of alkali metals (Jakse and Bretonnet 1993a, b). The reliability of the SMSA is equally well established by comparison with molecular dynamics (MD) simulations (Wax *et al* 1997).

We also take advantage of the adequacy of our model potential calculations in evaluating the electron–ion structure factor, $S_{ei}(q)$, that was obtained experimentally by Takeda *et al* (1986). If one knows the ionic structure factor $S(q)$, theoretical determination of $S_{ei}(q)$ is straightforward, and it can provide help in elucidating features of the screening electronic density, hidden in experimental results that are not sufficiently accurate yet. Moreover, it could explain why liquid Ga is a good electrical conductor (Ginter *et al* 1986) and presents a nearly-free-electron-like electronic structure (Indlekofer *et al* 1988), though exhibiting structural peculiarities.

This article is structured as follows. In its second section, we recall essential topics related to the determination of the effective ionic-pair potential from Shaw’s OMP and OB’s local-field correction. In the third section, the implementation of the ionic structure factor with the SMSA and of the electron–ion structure is explained. Our results are presented and discussed in section 4. Finally, we give our conclusions in section 5.

2. From electron–ion interaction to ion–ion interaction

Unlike local model potentials that, in a way, depend on adjustable parameters, non-local model potentials deal only with the spectrometric term energies of the free ion. In the present work, we use the non-local OMP proposed by Shaw (1968), which consists of a local coulombic electron–ion interaction plus a non-local part (we use atomic units, $\hbar = e = m = a_0 = 1$):

$$w_0(r, E) = -\frac{Z}{r} - \sum_{l=0}^{l_0} \Theta[R_l(E) - r] \left[A_l(E) - \frac{Z}{r} \right] \hat{P}_l$$

where $\Theta(r)$ is the unit step function, and \hat{P}_l denotes the projector on the l th angular momentum states of the core electrons. In this model, the well depths $A_l(E)$ and the radii $R_l(E)$ are related by the optimization condition $A_l(E)R_l(E) = Z$. The bare form factor is then given by

$$w_0(\mathbf{k}, \mathbf{q}) = N \langle \mathbf{k} + \mathbf{q} | w_0 | \mathbf{k} \rangle = v(q) + f(\mathbf{k}, \mathbf{q})$$

where

$$v(q) = -\frac{4\pi Z N}{q^2 V}$$

and

$$f(\mathbf{k}, \mathbf{q}) = -4\pi \frac{N}{V} \sum_{l=0}^{l_0} (2l+1) P_l(\cos \theta) \int_0^{R_l} j_l(k'r) \left[A_l(E) - \frac{Z}{r} \right] j_l(kr) r^2 dr.$$

According to Shaw (1970), the screened form factor can be written as the sum of the Hartree contribution and of the correction due to electron exchange and correlation effects, namely

$$w(\mathbf{k}, \mathbf{q}) = w_H(\mathbf{k}, \mathbf{q}) + \Delta w(\mathbf{k}, \mathbf{q})$$

where

$$w_H(\mathbf{k}, \mathbf{q}) = \frac{v(q) + v_d(q)}{\varepsilon_H(q)} + f(\mathbf{k}, \mathbf{q}) + g(q) \quad (1)$$

and

$$\Delta w(\mathbf{k}, \mathbf{q}) = -\frac{G(q)}{\varepsilon(q)} [w_H(\mathbf{k}, \mathbf{q}) - w_0(\mathbf{k}, \mathbf{q})].$$

Here, $\varepsilon_H(q)$ is Lindhard's dielectric function, and the many-electron effects are incorporated owing to the electron screening function

$$\varepsilon(q) = 1 + [1 - G(q)][\varepsilon_H(q) - 1]$$

where $G(q)$ is the local-field correction for the conduction electrons and depends on which type of treatment is adopted. We will come back later to the relative performances of different tractable forms of $G(q)$.

When evaluating the local contribution $v_d(q)$ due to the depletion hole ρ_d , we assume a uniform spatial charge distribution in a sphere of radius R_M , which leads to the relation

$$v_d(q) = \frac{4\pi N}{q^2 V} \rho_d M(q)$$

with

$$\rho_d = -\sum_{k < k_F} \langle \mathbf{k} | \frac{\partial w_0}{\partial E} | \mathbf{k} \rangle$$

and

$$M(q) = \frac{3}{q R_M} \left[\frac{\sin q R_M}{(q R_M)^2} - \frac{\cos q R_M}{q R_M} \right]$$

where $R_M = (R_0 + 3R_1 + 5R_2)/9$ is a weighted mean of the core radii R_i . The depletion hole is a consequence of the energy dependence of the model potential, and the modulating function $M(q)$ takes into account its spatial distribution. When omitted, the form factor exhibits oscillations at large q that produce an unphysical interionic pair potential.

The last term of equation (1) represents the non-local screening contribution

$$g(q) = \frac{4}{\pi^2 q^2 \varepsilon_H(q)} \int \frac{f(\mathbf{k}, \mathbf{q})}{k^2 - |\mathbf{k} + \mathbf{q}|^2} d\mathbf{k}.$$

Table 1. Values of the quantities used in this work. Atomic units are used. The parameters A_l of Shaw's OMP are given at the Fermi energy. Z^* , m_E , and m_k are respectively the effective valence and the two effective masses as defined in the text, while k_F , Ω_0 , and T have their usual meaning.

A_0	A_1	A_2	dA_0/dE	dA_1/dE	dA_2/dE
1.601	1.854	1.522	-0.386	-0.220	0.015
k_F	T	Ω_0	Z^*	m_E	m_k
0.8748	323	132.694	3.1846	0.9447	0.7430

In deriving an expression for the ion–ion interaction by standard pseudopotential theory, it is necessary to define the scalar function $F_N(q)$, called the normalized energy–wavenumber characteristic, which is written similarly to the screened form factor as

$$F_N(q) = F_N^H(q) + \Delta F_N(q)$$

with

$$F_N^H(q) = - \left[\frac{q^2}{4\pi Z^*} \frac{V}{N} \right]^2 \left\{ \left[\frac{1 - \varepsilon_H(q)}{\varepsilon_H(q)} \right] [v(q) + v_d(q)]^2 + g(q) [v(q) + v_d(q)] + \varepsilon_H(q) g^2(q) + h(q) \right\}$$

and

$$\Delta F_N(q) = \left(\frac{q^2}{4\pi Z^*} \frac{V}{N} \right)^2 \frac{\varepsilon_H(q)}{\varepsilon(q)} G(q) [w(\mathbf{k}, \mathbf{q}) - w_0(\mathbf{k}, \mathbf{q})]^2$$

where

$$h(q) = \frac{4}{\pi^2 q^2} \int_{k \leq k_F} \frac{f^2(\mathbf{k}, \mathbf{q})}{k^2 - \|\mathbf{k} + \mathbf{q}\|^2} d\mathbf{k}.$$

The OMP is not transferable and some care must be taken with its energy dependence. Thus, the well depths $A_l(E)$ have to be determined at the observed temperature and density of the liquid metal. We followed the procedure proposed by Ese and Reiland (1973) to obtain them. In addition, our calculations include the two masses m_E and m_k , which are a consequence of the energy dependence and of the non-locality, respectively. These masses, appearing as renormalization factors in the dielectric function and in the depletion hole, have been found to give rise to sensible corrections in the screened form factor and in the normalized energy–wavenumber characteristic (Bretonnet and Regnaut 1985). Within OMP theory, it turns out that m_E can be incorporated in the effective valence $Z^* = Z - \rho_d/m_E$. The values of the quantities entering all of these formulae and used in this work are summarized in table 1.

Finally, the interionic potential $u(r)$ can be readily obtained as the sum of a direct ion–ion interaction and of an indirect contribution stemming from the presence of the electron gas:

$$u(r) = \frac{Z^{*2}}{r} \left[1 - \frac{2}{\pi} \int_0^\infty F_N(q) \frac{\sin qr}{q} dq \right].$$

At this stage of the presentation of the OMP, it is convenient to give the Fourier transform of the screening electron density around an ion that will be necessary for the calculation of the electron–ion correlations:

$$n_{sc}(q) = \frac{q^2}{4\pi} \frac{\varepsilon_H(q)}{\varepsilon(q)} [w_H(\mathbf{k}, \mathbf{q}) - w_0(\mathbf{k}, \mathbf{q})]. \quad (2)$$

Now, we come to the question of the local-field correction. Since the simplest form of the dielectric function $\varepsilon_H(q)$ suffers from the absence of exchange–correlation effects, which are found to have a great influence on the liquid structure, we must include them properly by means of the function $G(q)$. Many expressions for $G(q)$ have been proposed in the literature, even recently (Moroni *et al* 1995, Richardson and Ashcroft 1994), but here we focus on just three of them: the local-field functions of Vashishta and Singwi (1972) (VS), of Ichimaru and Utsumi (1981) (IU) and of OB. The first two, known to satisfy the self-consistency conditions in the compressibility sum rule for the uniform electron

gas, are tractable and have been extensively used during the last decade. The third local-field correction is drawn from the calculations of Ortiz and Ballone (1994) based on the latest developments of the quantum Monte Carlo method that provide a very sophisticated description of the many-body properties of the homogeneous electron gas. Bretonnet and Boulahbak (1996) proposed the following analytical form for the OB $G(q)$:

$$G(q) = 1 - g(0) - \exp(-z) \sum_{n=0}^6 C_{\mu 1} F_1(1 - \mu/2, 3/2, z)$$

where

$$z = \frac{1}{4} \left(\frac{9\pi}{4} \right)^{2/3} \frac{q^2}{ak_F^2}$$

and

$$C_0 = \frac{B}{2} \sqrt{\pi/a}$$

$$C_1 = \frac{C - aA}{a}$$

$$C_2 = \frac{3D - 2aB}{4} \sqrt{\pi/a^3}$$

$$C_3 = \frac{2E - aC}{a^2}$$

$$C_4 = \frac{3}{8} (5F - 2aD) \sqrt{\pi/a^5}$$

$$C_5 = -\frac{2E}{a^2}$$

$$C_6 = -\frac{15}{8} F \sqrt{\pi/a^5}.$$

All relevant parameters are given in table 1 of their paper. The degenerate hypergeometric function ${}_1F_1(1 - \mu/2, 3/2, z)$ has to be implemented up to the eighth order in z , so that the stability of $G(q)$ is reached. Incidentally, it is easy to see that the present expression for $G(q)$ can be written in a form recalling that of VS, when the degenerate hypergeometric function is developed.

3. Ion-ion and electron-ion correlation functions

We now outline the steps followed in obtaining a good approximation to the correlations in liquid Ga whose ions interact via the effective pair potential given in section 2. The integral equation under consideration is based on a combination of the Ornstein-Zernicke relation

$$g(r) - 1 = c(r) + \rho \int [g(r) - 1] c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'$$

with the auxiliary equation of the SMSA for the direct correlation function

$$c(r) = \{1 - \exp[\beta u_1(r)]\} g(r) - \beta u_2(r).$$

It has been shown (Madden and Rice 1980) that the SMSA is an integral equation particularly appropriate for dense fluids interacting with Lennard-Jones potentials or with potentials for liquid metals, if the decomposition of the potential $u(r)$ is that of Andersen

et al (1972). In effect, for continuous potentials, it is well recognized that the most useful separation must be done at the position of the first potential minimum r_0 :

$$u_1(r) = \begin{cases} u(r) - V_{min} & \text{if } r < r_0 \\ 0 & \text{if } r > r_0 \end{cases}$$

and

$$u_2(r) = \begin{cases} V_{min} & \text{if } r < r_0 \\ u(r) & \text{if } r > r_0. \end{cases}$$

The reason for the success of this decomposition lies in the fact that $u_1(r)$ gives rise to a purely repulsive force responsible for the packing constraints on the arrangement of ions, while $u_2(r)$ corresponds to a long-range one that greatly influences the thermodynamics.

It is worth mentioning that the SMSA does not involve any variational parameter or mixing function ensuring thermodynamical consistency. As a first consequence, the only unambiguous test to which we can subject this integral equation is the comparison of its structure factor results with those of simulation for the same effective pair potential. Secondly, the SMSA does not allow one to determine the thermodynamic properties of the actual system, in contrast to, for instance, the hybridized mean-spherical approximation (Bretonnet and Jakse 1992). Here, we did not use such an alternative improved integral equation requiring the knowledge of the internal energy or of the pressure, for the simple reason that the calculation of the volume-dependent energy with the non-local OMP of Shaw is intractable.

To gain precision and save time, we use the combination of the Newton–Raphson and the successive-substitution methods, proposed by Labik *et al* (1985), for solving the integro-differential equation set. This procedure, presented by Bretonnet and Jakse (1994), has already demonstrated its rapidity and its efficiency.

Once the ion–ion pair correlation function is obtained with the SMSA, the ionic structure factor can be calculated by Fourier transformation:

$$S(q) = 1 + \rho \int [g(r) - 1] e^{iqr} dr. \quad (3)$$

In fact, pure liquid metals are known to be binary mixtures of ions and electrons, and it is well established that both ion–ion and electron–ion structure factors can be determined from neutron scattering and x-ray diffraction experiments if they are carried out with sufficient accuracy (Egelstaff *et al* 1974). Since recent improvements were made in these techniques, several experimental determinations of electron–ion correlation have been published by a Japanese group, especially for liquid Ga (Takeda *et al* 1986). On the other hand, there have been some theoretical approaches to the correlation functions for ions and electrons in liquid metals (Hoshino and Watabe 1992, Chihara 1987). It turns out that the information contained in the electron–ion correlation refers equally to the screening electron density $n_{sc}(q)$ and the ionic structure factor $S(q)$, which must be determined in a self-consistent way. Within the linear screening approach, the electron–ion pair correlation function $g_{ei}(r)$ and the electron–ion structure factor $S_{ei}(q)$ are given by (Cusack *et al* 1976, Hoshino and Watabe 1992)

$$g_{ei}(r) = 1 + \frac{Z^{1/2}}{\rho} \frac{1}{8\pi^3} \int S_{ei}(q) e^{iqr} dq$$

and

$$S_{ei}(q) = Z^{-1/2} n_{sc}(q) S(q)$$

where $n_{sc}(q)$ and $S(q)$ are those of equation (2) and equation (3), respectively. Theoretical determination of $g_{ei}(r)$ can thus provide a useful comparison with experiments, although certain precautions must be taken when analysing the curve of $g_{ei}(r)$ in the core region, since the pseudo-wave-function is used instead of the actual wave-function in the model potential theory. So, the charge density calculated within the cores with this formalism is not the real one, but a pseudo-density.

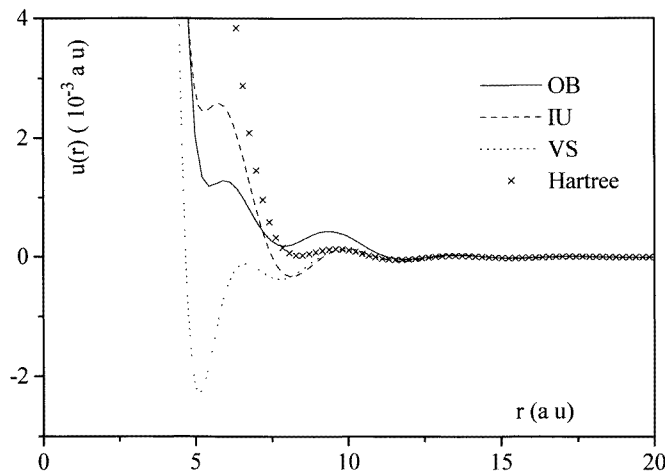


Figure 1. Interionic pair potentials obtained with the three dielectric functions considered. Hartree's screening does not include any exchange or correlation effect.

4. Results and discussion

In figure 1, we show the sensitivity of the pair potential to three different local-field functions. Among them, two have been extensively used for simple metals—namely, the screening function of VS, which has the virtue of satisfying the self-consistency conditions over the entire range of metallic densities, and that of IU that reproduces the Monte Carlo results. In addition, the third local-field function, discussed in section 2 and referred to as the OB function, is used for the first time in the present form (Bretonnet and Boulahbak 1996). It is worth mentioning that most local-field corrections are significantly different from one another, especially beyond k_F (figure 2). This non-uniqueness of $G(q)$ is the mark of our ignorance about the exact nature of the exchange–correlation effects within the uniform electron gas. Such differences in $G(q)$ are responsible for the great uncertainty concerning the interionic potential in the region around the first and second neighbours.

Going from one to another local-field function significantly changes the character of the potential in the range 5 to 10 a.u. for Ga. The features of the potentials with VS's and IU's local-field functions are now well known, with a first-minimum depth considerably smaller for IU's than for VS's screening. With OB's local-field function, the interesting point to be noted is a surprisingly unconventional pair potential with two positive first minima located at 5 and 8 a.u., respectively. Comparing the potentials corresponding to IU's function and OB's function, one notices a similar first minimum and an identical sign for du/dr between the first two minima. As will be seen later, this behaviour drastically modifies the profile of the main peak of $S(q)$. For Ga, having a low melting point, the weak ionic kinetic energy

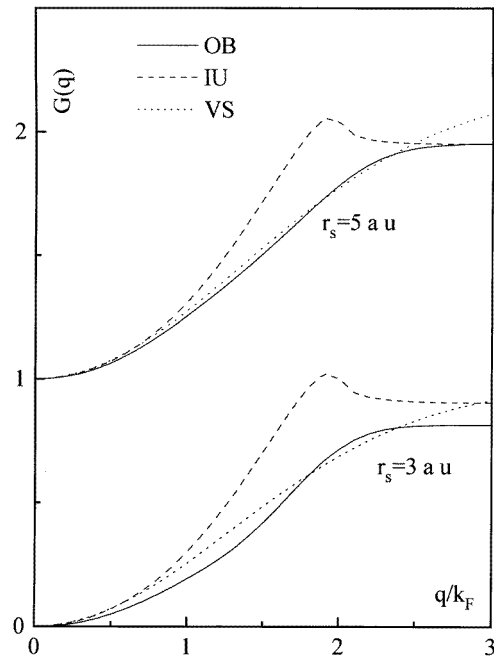


Figure 2. Local-field corrections $G(q)$ evaluated following various schemes. The parameter r_s is the radius of the average volume per electron, and its value is 2.1939 au for Ga.

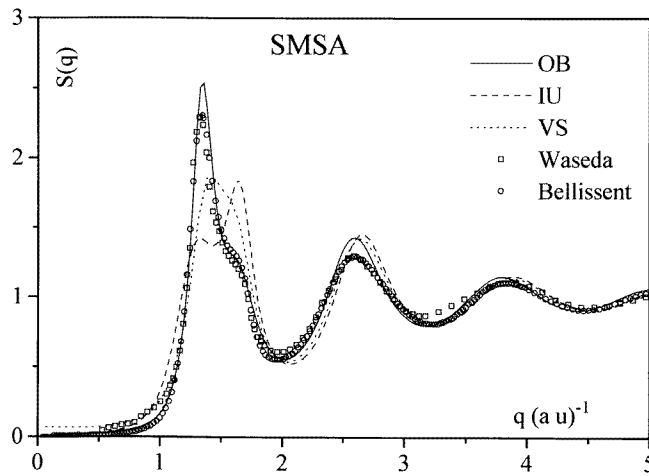


Figure 3. Ionic structure factors obtained using the three dielectric functions mentioned, and compared with the experimental results of Waseda (1980) and of Bellissent-Funel *et al* (1989).

($\frac{3}{2}k_B T \simeq 1.5 \times 10^{-3}$ au if $T = 300$ K) is not always sufficient to overcome such potential barriers and, therefore, the liquid structure is very sensitive to the shape of the ion–ion potential in that region.

The impact of the different interionic potentials on the ionic structure factor, when calculated using the SMSA, is clearly illustrated in figure 3. Important differences appear

over the whole q -range, but they are more pronounced in the first-peak region. This is specific to Ga, since in the cases of alkali metals or of Al, the influence of $G(q)$ is sensitive only in the low- q region of $S(q)$. Both VS's and IU's screenings give rise to first peaks of $S(q)$ whose shapes are greatly different from experimental results. Such shapes were already observed by Bretonnet and Regnaut (1985). On the other hand, OB's screening function allows one to reproduce remarkably well the shoulder on the main peak of $S(q)$, leaving the amplitudes of the oscillations and of the first peak still uncertain.

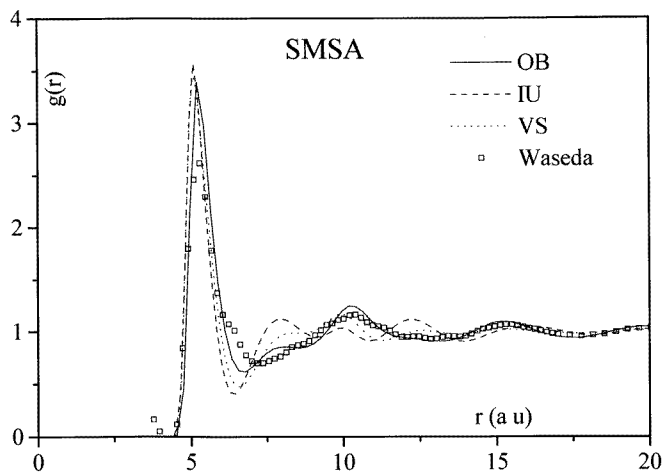


Figure 4. Ionic pair distribution functions obtained with the SMSA and the three dielectric functions mentioned, and compared with Waseda's experimental results (Waseda 1980).

We now turn to examining the pair correlation function calculated with the SMSA, for the three interionic potentials under consideration (figure 4). The positions and heights of the first peak are similar for the three screening functions, and the differences occur mainly in the phase of the oscillations. It is not surprising to observe the strong change beyond the first peak, for the simple reason that it corresponds to the region where the potential is affected by the exchange-correlation effects. As far as the agreement between theory and experiment is concerned, one can easily see that the curve stemming from the OB function fits the second and third peaks of $g(r)$ fairly well. The remaining part of the curve, and in particular the range between the first two peaks, is not satisfactorily predicted, although OB's screening seems to give the best results. This indicates the great difficulty encountered in describing and explaining the properties of Ga.

In fact, there is the standard question of the validity of the results when obtained with an approximate integral equation. A useful test of the approximation can be realized if they can be compared with some 'exact results' from computer experiments based on the same realistic interionic potential. Therefore, we performed MD simulations of liquid Ga with the same potentials (figure 5). A comparison of the MD and SMSA results with experiment shows that both IU's and VS's results have worsened while OB's results are quite stationary when using MD. This confirms the fact that OB's screening gives better results than both of the others.

The improved agreement of the experimental structure factor and that calculated with OB's function emphasizes the importance of using a realistic dielectric function. As regards the remaining disparities in $S(q)$, irrespective of the agreement that we have obtained with

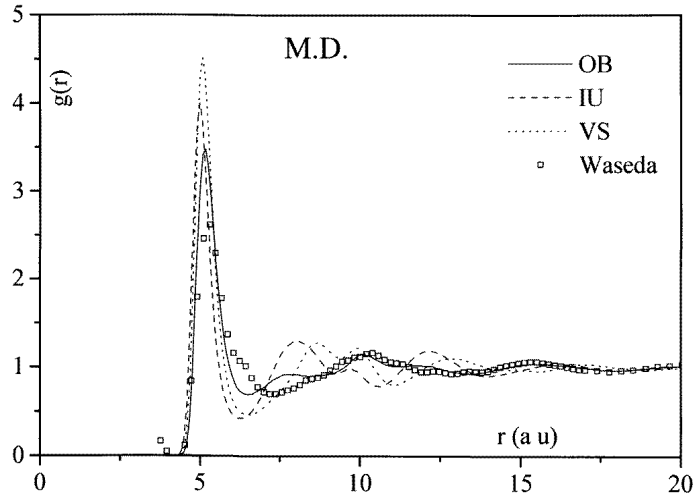


Figure 5. Ionic pair distribution functions obtained with MD and the three dielectric functions mentioned, and compared with Waseda's experimental results (Waseda 1980).

the new local-field function of OB, we cannot, unfortunately, provide a definitive judgment.

Now, coming to the electron–ion correlation, we take advantage of both the electronic screening density and ionic structure factor to determine the electron–ion structure factor $S_{ei}(q)$, which describes the correlation between the local density of electrons and that of ions. As recalled in section 3, a reliable determination of the electron–ion correlation in liquid metals is, in principle, possible by combining high-resolution measurements performed with the neutron scattering and x-ray diffraction methods. Recent progress in these diffraction techniques has motivated some investigators (Takeda *et al* 1986) to carry out an experimental determination of $S_{ei}(q)$ for Ga. However, care must be taken when dealing with these results, since the indicated experimental uncertainty ($\Delta S_{ei} = \pm 0.2$) is, in the case of Ga, of the order of the amplitude of the long-range oscillations and of half the height of the first peak. Consequently, the delicate experimental determination of electron–ion correlation in liquid metals is especially difficult in the case of liquid Ga, and these results can only be considered as indicative.

Since the determination of $S_{ei}(q)$ requires the knowledge of the electronic screening density, $n_{sc}(q)$, and of the ionic structure factor, $S(q)$, we performed the calculations of $S_{ei}(q)$ in a consistent manner, with $S(q)$ and $n_{sc}(q)$ determined with the same screening. We have plotted $n_{sc}(q)$ and $S_{ei}(q)$ in figure 6. While for $n_{sc}(q)$ the particular screening function used seems immaterial, $S_{ei}(q)$ is very sensitive to the choice of $G(q)$, and this is mainly due to $S(q)$. The curves for $S_{ei}(q)$ obtained show a sharp positive peak followed by a small negative minimum. They are quite different from those obtained for alkali metals by Wax *et al* (1997), who followed the same approach. If we compare our results with the experiments of Takeda *et al* (1986), the curves appear to be very different. This is not surprising, in view of the high value of the experimental uncertainties. This has already been pointed out by Ishitobi and Chihara (1992), who demanded a better accuracy in the experimental determination of $S_{ei}(q)$, so as to be able to discuss their analytical results. Moreover, it is worth mentioning that, in order to refine their experimental results for Mg, Takeda *et al* (1994) applied the back-Fourier-transform technique to smooth the curve and damp the spurious oscillations. The corrected curve appears then to be very different from

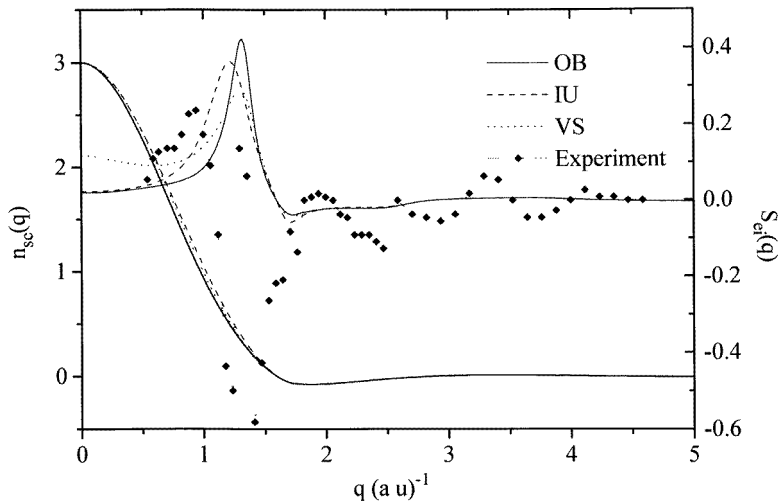


Figure 6. The reciprocal screening charge density $n_{sc}(q)$ and electron-ion structure factor $S_{ei}(q)$ for three types of dielectric screening. The experimental results of Takeda *et al* (1986) are shown for information. The experimental uncertainty reported by these authors is $\Delta S_{ei} = \pm 0.2$.

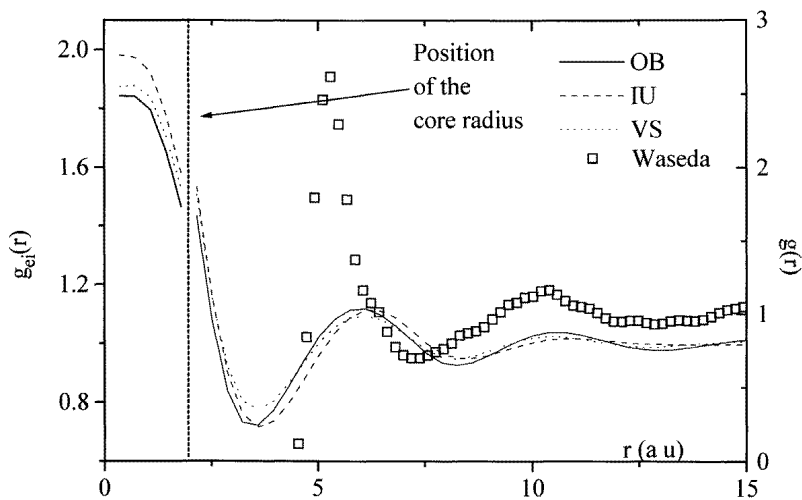


Figure 7. Calculated electron-ion pair distribution functions $g_{ei}(r)$ obtained using three dielectric functions, and the experimental ionic pair distribution function from Waseda (1980).

the unrefined one and has a shape very similar to our calculated one for Ga. Consequently, we should not reject our results simply on the basis of a comparison of them with their unrefined experimental counterparts.

To get better insight into the electron-ion correlation, we present $g_{ei}(r)$ and $g(r)$ in figure 7. An important point that we have to remember is that, since $g_{ei}(r)$ is calculated with the pseudo-wave-function associated with the pseudopotential, it has no real meaning inside the core, since the pseudo-wave-function departs from the true one in the core volume. Furthermore, the use of an energy-dependent potential introduces a depletion hole charge

localized in the ion core. We supposed it to be uniformly distributed within a core radius $R_M = 1.84$ au. Therefore, a discontinuity of $g_{ei}(r)$ appears at $r = R_M$ that reflects the step function used to describe the distribution of the depletion hole charge in the core. So, we have to concentrate in our discussion on the part of the curve corresponding to $r > R_M$. First, we can notice that, though $S_{ei}(q)$ is very sensitive to $G(q)$, $g_{ei}(r)$ is rather less affected by it. But the most striking feature is the fact that, contrary to what happens in the case of alkali metals, the maximum of $g(r)$ does not coincide with the first minimum of $g_{ei}(r)$, but rather with its first peak. This means that the valence electrons are located at distances that correspond to the position of the first ionic neighbours. It seems rather improbable that electrons are concentrated inside the ionic cores, and we envisage two possible explanations of this peculiarity of the electron–ion structure. The first one is built up from an experimental observation by Gramsch *et al* (1991), who interpreted their positron annihilation measurements for liquid Ga as being a consequence of the creation of trapping centres on melting, though the real nature of these traps is not currently understood. So, electrons could occupy such interstitial volumes. The second one involves consideration of the fact that Ga cores carry a charge three times higher than that carried by the alkali ones. Consequently, they are more attractive, and electrons are closer to the cores. What we observe would not be electrons inside the cores, but rather electrons ‘stuck’ around them. Nevertheless, our results remain surprising, and require further experimental, as well as theoretical, investigations before they can be considered as confirmed.

5. Conclusion

The purpose of the present investigation was to predict the anomalies of the ionic structure of liquid Ga. It turns out that the use of the OMP with the OB local-field function provides a reliable interionic potential capable of giving the structure factor with a very good agreement. The calculations are done in the context of a non-local model potential, and do not represent an attempt to obtain the best agreement with experiment by means of adjustable parameters.

There are, however, noticeable deviations from the experimental pair correlation functions in the range between the two first peaks. The difficulty in reproducing $g(r)$ in that range may have several explanations.

(i) The possible drawbacks of the OMP—although this model potential, based on firm theoretical foundations, is an optimized potential incorporating full non-locality and energy dependence. It has shown a great ability to reproduce numerous physical properties for solid and liquid metals in the course of the last two decades. We put much faith in it.

(ii) Lacking terms in the interionic potential: in view of the paper of Mon *et al* (1979), one may anticipate that the interionic potential of Ga should be augmented with a term reflecting the core–core exchange repulsion, which can be sufficiently well approximated by the Born–Mayer potential, and another term corresponding to the core–valence exchange contributions. However, according to Dharma-wardana and Aers (1983), no significant improvement in the quality of $S(q)$ is obtained for Al when such terms are included. At this time, it is not possible for us to judge the relative merit of these contributions.

(iii) The inaccuracy of the local-field function: the form of the interionic potential is very sensitive to the details of the structure of the homogeneous electron gas. Our results show that the improved self-consistent treatment of many-electron correlation effects due to OB brings the calculated structure of Ga into better agreement with experiments than the other local-field functions. Effort devoted to reconsideration of the screening effects together with exchange–correlation effects seems to be the way to improve this agreement.

Our complementary study of the electron-ion correlation gives interesting results. Though a comparison with experiment is difficult because of experimental uncertainties, and even if the determination of $g_{ei}(r)$ is valid only for $r > R_M$ because of formalism requirements, our calculations have pointed out an outstanding feature. Indeed, it appears that $g_{ei}(r)$ has a maximum at the position of the first peak of $g(r)$. This striking property requires confirmation by other investigations of both experimental and theoretical kinds, but it could be interpreted, following Gramsch *et al* (1991), in terms of interstitial free volumes that electrons could occupy.

Acknowledgment

The CIRIL (Centre Interuniversitaire de Ressources Informatiques de Lorraine), where some of the numerical calculations were performed, is gratefully acknowledged for providing us with computer time.

References

- Andersen H C, Chandler D and Weeks J D 1972 *J. Chem. Phys.* **56** 3812
 Bellissent-Funel M C, Chieux P, Levesque D and Weis J J 1989 *Phys. Rev. A* **39** 6310
 Bizid A, Bosio L, Curien H, Defrain A and Dupont M 1974 *Phys. Status Solidi a* **23** 135
 Bretonnet J L and Jakse N 1992 *Phys. Rev. B* **46** 5717
 ———1994 *Phys. Rev. B* **50** 2880
 Bretonnet J L and Boulahbak M 1996 *Phys. Rev. B* **53** 6859
 Bretonnet J L and Regnaut C 1985 *Phys. Rev. B* **31** 5071
 Chihara J 1987 *J. Phys. F: Met. Phys.* **17** 295
 Cusack S, March N H, Parrinello M and Tosi M P 1976 *J. Phys. F: Met. Phys.* **6** 749
 Dharma-wardana M W C and Aers G C 1983 *Phys. Rev. B* **28** 1701
 Egelstaff P A, March N H and McGill N C 1974 *Can. J. Phys.* **52** 1651
 Ese O and Reisland J A 1973 *J. Phys. F: Met. Phys.* **3** 2066
 Ginter G, Gasser J G and Kleim R 1986 *Phil. Mag.* **B 54** 544
 Gramsch E, Lynn K G, Throwe J and Kanazawa I 1991 *Phys. Rev. Lett.* **67** 1282
 Hafner J and Jank W 1990 *Phys. Rev. B* **42** 11 530
 Hoshino K and Watabe M 1992 *J. Phys. Soc. Japan* **61** 1663
 Ichimaru S and Utsumi K 1981 *Phys. Rev. B* **24** 7385
 Indlekofer G, Oelhafen P, Lapka R and Güntherodt H J 1988 *Z. Phys. Chem., NF* **157** 465
 Ishitobi M and Chihara J 1992 *J. Phys.: Condens. Matter* **4** 3679
 Jakse N and Bretonnet J L 1993a *Phys. Status Solidi b* **176** 299
 ———1993b *J. Non-Cryst. Solids* **156–158** 149
 Labik S, Malijevsky A and Vonka P 1985 *Mol. Phys.* **56** 709
 Madden W G and Rice S A 1980 *J. Chem. Phys.* **72** 4208
 Mon K K, Ashcroft N W and Chester G V 1979 *Phys. Rev. B* **19** 5103
 Moroni S, Ceperley D M and Senatore G 1995 *Phys. Rev. Lett.* **75** 689
 Ortiz G and Ballone P 1994 *Phys. Rev. B* **50** 1391
 Regnaut C, Dupont M and Badiali J P 1980 *J. Physique C8* 603
 Richardson C F and Ashcroft N W 1994 *Phys. Rev. B* **50** 8170
 Shaw R W 1968 *Phys. Rev.* **174** 769
 ———1970 *J. Phys. C: Solid State Phys.* **3** 1140
 Takeda S, Harada S, Tamaki S and Waseda Y 1986 *J. Phys. Soc. Japan* **55** 3437
 Takeda S, Inui M, Tamaki S, Maruyama K and Waseda Y 1994 *J. Phys. Soc. Japan* **63** 1794
 Vashishta P and Singwi K S 1972 *Phys. Rev. B* **6** 875
 Waseda Y 1980 *The Structure of Non-Crystalline Materials* (New York: McGraw-Hill)
 Wax J F, Jakse N and Bretonnet J L 1997 *Phys. Rev. B* at press