Electron-Ion Correlation in Liquid Metals from First Principles: Liquid Mg and Liquid Bi

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We present a theoretical determination of electron-ion pair correlation functions g_{ie} in liquid Mg and liquid Bi, two systems with widely different electronic and cohesive properties. Our calculations are based on first-principles molecular-dynamics simulations, which provide an accurate and mutually consistent description of the atomic and electronic structures of these systems. Our results show that g_{ie} exhibits substantially different features in Mg and Bi liquids. For liquid Mg, g_{ie} clearly reflects the delocalization of the valence atomic charge related to metallic bond formation. In the case of Bi, instead, the spherical average implicit in g_{ie} does not allow it to reveal the existence of transient directional bonds which are an important feature of the charge density in this liquid.

Liquid metals can be described as mixtures of electrons and ions. Some of the electrons (the core electrons) remain very close to the nuclei and are negligibly affected by the atomic motion. The remaining electrons (valence electrons) are mobile through the assembly of ions and are responsible for the transport as well as the cohesive properties of the liquid metal.

Neutron, x-ray, and electron scattering can be used to probe the structure of the liquid. With these methods, the scattering intensities are determined, respectively, by the nuclear density-density, the electron density-density, and the charge density-density correlation functions. Already many years ago, Egelstaff, March, and McGill [1] realized that it is in principle possible to obtain electron-ion pair correlations by combining high resolution measurements performed with the three different methods. A reliable determination of these electron-ion correlations in liquid metals is of considerable interest, since they provide the only experimental access to the electron density, which is a main ingredient of our present understanding of the electronic properties, but cannot be directly obtained from experiments. The electron-ion pair correlation function g_{ie} describes the correlation between the local density of the electrons and the local density of the ions according to

$$g_{ie}(r)\rho_i n_0 \Omega = \left\langle \sum_{j=1}^{N} n(r + R_j) \right\rangle, \qquad (1)$$

where ρ_i denotes the average number density of ions, $n(r)$ is the density of electrons (n_0 is the average), R_j denote the ionic positions, Ω stands for the volume that is occupied by N ions, and $\langle \cdots \rangle$ denotes the configurational average. The definition of the corresponding electron-ion structure factor $S_{ie}(q)$ can be made in the usual Ashcroft-Langreth way (see, e.g., [2]). Of course, in a liquid g_{ie} and S_{ie} depend only on the modulus of r and q, respectively.

Theoretical work following the pioneering paper by Egelstaff, March, and McGill gave general results [3,4],

although mainly in the regime of validity of linear response theory, and suggested that $g_{ie}(r)$ could be obtained by using x-ray and neutron scattering only, in combination with homogeneous electron gas expressions for electron-electron correlations [4]. Recent progress in x-ray and neutron diffraction techniques has motivated attempts at such an analysis. Experimental determinations of g_{ie} have been published for liquid Bi and Sn [5], Al [6], Na [7], Ga and Tl [8], Zn and Pb [9], and Mg [10]. However, experimentally g_{ie} is essentially obtained as the small difference of two relatively large functions (the x-ray and neutron radial distribution functions), and its accuracy is strongly dependent on the quality of both these functions. Since the latter cannot be derived from the raw data without large corrections for systematic errors, which are rather different for neutron and x-ray diffraction, the resulting uncertainties in the experimental g_{ie} are quite large. For this reason, theoretical determinations of g_{ie} can provide a useful comparison with (check-on) experiments, and also help in elucidating important features of g_{ie} which are not revealed by experiments, e.g., its relation to the electronic charge distribution in the liquid metal.

In this Letter we get insight into the behavior of g_{ie} in two widely different liquid metals like Mg and Bi by means of accurate calculations using the Car-Parrinello *ab initio* molecular-dynamics method [11]. This scheme, allowing one to perform molecular dynamics (MD) with interactions derived from a local density functional (LDF) calculation of the electronic density, is naturally tailored to deal with this problem. Note that by definition the information contained in g_{ie} equally refers to the electronic density and ionic distribution, which must be thus determined in a consistent way. Two reasons motivated us to choose the Mg and Bi liquids. First, for both systems a determination of g_{ie} from experiment is available [5,10]. In addition, there is an important difference in the nature of the behavior of the valence electrons in these two elements. Mg is a good metal

with nearly free electrons. Bi is instead in the solid state a semimetal with a high degree of localization of the valence electrons. It is therefore important to compare the two cases as prototypes of two extreme behaviors. We find that for Mg g_{ie} directly reflects the rearrangement of the valence atomic charge, related to the formation of metallic bonds in the liquid. For liquid Bi, instead, g_{ie} is very similar to the pair correlation corresponding to a superposition of atomic charge densities, since the spherical average implicit in Eq. (1) does not allow it to reveal the presence of transient directional bonds which are formed in this liquid. The different features of g_{ie} in these two systems allow one to clearly distinguish a nearly free electron (NFE) metal like liquid Mg (l-Mg) from a "bad metal" like liquid Bi (l-Bi).

Like Takeda *et al.* we only consider correlations between the valence electrons and the Mg^{2+} or Bi^{5+} ions. In our calculations, however, $n(r)$ will be the pseudocharge instead of the real charge density. Consequently, the actual shape of the charge density at the atomic cores is not accurately given by our calculation. This inaccuracy, however, concerns a region of radius ~ 1.3 a.u. around the atomic nuclei, and has no consequence on the charge density at larger distances, namely, in the region interesting for cohesive properties. Here the adequacy of LDF pseudopotential calculations for accurately describing the valence charge distribution is well established (see, e.g., [12]).

Calculations have been carried out at constant density in a periodically repeated simple cubic box containing 90 Mg or 60 Bi atoms. The (valence) electronic states were sampled at the Γ point only, and expanded in plane waves with a kinetic energy cutoff of 12 Ry [13]. The electron-ion interactions were described by norm-conserving pseudopotentials [14], in a separable form [15]. Details of testing these potentials are given elsewhere [16]. During the production runs the adiabatic evolution of the wave functions and a canonical sampling by the ionic trajectories were realized by means of two Nosé thermostats according to the method from Ref. [17].

In order to avoid the long equilibration times required by starting from a crystalline arrangement, the initial configurations, for both l-Mg and l-Bi, were derived from a configuration of our recent simulation of the Mg_3Bi_2 alloy [16]. The atomic structure of this liquid alloy is very different from that of both l-Mg and l-Bi, ensuring that our results are not biased by the choice of initial conditions. The density was set equal to the experimental density at 1000 and 573 K [2] for l-Mg and l-Bi, respectively. The 90 atom Mg sample was heated to about 1400 K and then cooled down to a temperature of 1000 K. The equilibration period lasted for 2.9 ps. The production run lasted for 1.8 ps. Equilibration of the 60 atom l-Bi sample was started at 1000 K and continued at this temperature for 3.5 ps. During this equilibration we realized that cooling down to the

experimental melting point of 544 K [18] would slow down the diffusion of the atoms so much that it would make the computational effort exceedingly large. We thus maintained the simulation temperature at 1000 K. This leaves a small error in the length of the simulation box ($\sim 2\%$). The production run lasted for 4.15 ps.

First we present our results for l-Mg. Figure 1 (upper panel) depicts the Mg structure factor and compares it to experiment at 953 K [2]. In the same figure the comparison in real space is made. The agreement between theory and experiment is clearly very good. Integrating $g(r)$ to 4.3 Å a coordination number of 12.2 is extracted, a value typical of a hard-sphere-like system.

In the middle part of Fig. 1 the solid lines depict plots of both g_{ie} and S_{ie} obtained as an average over eight instantaneous configurations generated during our simulation. $g_{ie}(r)$ has a clear maximum at about 1.25 Å followed first by a rather broad tail and next by an oscillatory decay.

To get better insight into the behavior of $g_{ie}(r)$, we introduce the functions $g_{ie,0}(r)$ and $S_{ie,0}(q)$, which are, respectively, the electron-ion pair correlation function and structure factor as obtained from a sum of spherically symmetric free-atom (pseudo)charge densities centered on all the ions (for the same eight atomic configurations). These functions are also shown in the middle panels of Fig. 1 (dashed lines). The lower part of Fig. 1 shows the difference correlation functions, e.g., $g_{\text{diff}} = g_{ie} - g_{ie,0}$. A depletion of charge on the nuclei at the central atom and the atoms of the first and second coordination shells is evident when $g_{\text{diff}}(r)$ is compared to the atomic $g(r)$.
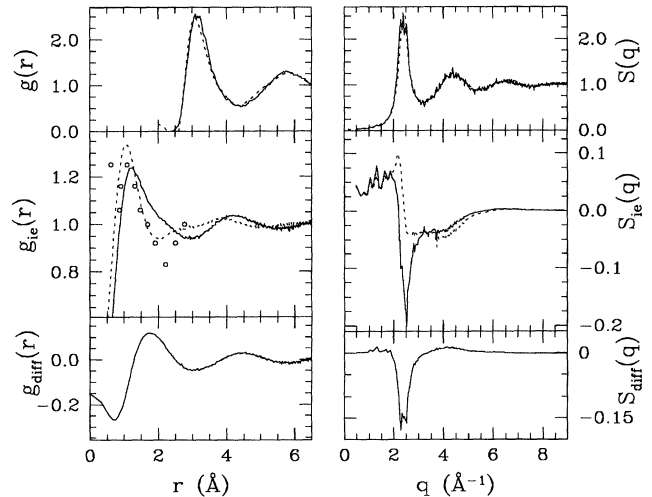

FIG. 1.   Mg correlation functions. Top panels show $g(r)$ and $S(q)$. The solid line is the simulation result, the dotted line pertains to experiment [2]. In the middle, the left panel shows g_{ie} (solid line) and $g_{ie,0}$ (dotted line), and the right panel shows S_{ie} (solid line) and $S_{ie,0}$ (dotted line). The circles are experimental points from Ref. [10]. The lowest panels show the difference correlation functions, i.e., $g_{\text{diff}} = g_{ie} - g_{ie,0}$.

The negative peak in S_{diff} at 2.5 Å^{-1} corresponds to the typical distance between two depletion areas: $7.7/2.5 = 3.1$ Å [19]. A further comparison of $g_{diff}(r)$ and $g(r)$ reveals that charge accumulates in the area in between the Mg atoms. The main maximum of g_{diff}, however, is not located at half the distance from the central atom to the first neighbor shell, but slightly beyond (in the broad tail of g_{ie}). This is clarified by direct analysis of the charge density $n(r)$ in the liquid. Contour plots of $n(r)$ and of the difference $n_{diff}(r)$ between $n(r)$ and the superposition of atomic charge densities are plotted in Fig. 3 (upper panels) for a typical configuration of l-Mg. From this figure it is apparent that a metallic, i.e., multicentered, bonding occurs. Therefore the difference charge density maxima are located beyond half the average nearest-neighbor distance.

Next we examine l-Bi. In Fig. 2 we compare the structure factor as obtained from the simulation at 1000 K to the experimental structure factor by Knoll, Lamparter, and Steeb [20]. In the region of the main peak our data are rather noisy, however, the overall agreement between experiment and simulation is remarkably good. In the same figure the pair distribution function $g(r)$ is compared to the experimental results [20]. Note that the main peak of $g(r)$ as obtained from the simulation is sharper than the main peak as obtained by the experiments. Following

Li [21], we broadened our data with the experimental resolution [22]. The resulting $g(r)$ (dashed line) is almost on top of the experimental $g(r)$. As no clear minimum is present after the main peak of $g(r)$ (at ~3.25 Å), the coordination number is not well defined. It is, however, informative to consider the running coordination $z(R)$ obtained by integrating $g(r)$ up to R: $z(R) = 2.6, 4.8, 6.2$, and 7.9 for cutoffs R of 3.25, 3.5, 3.75, and 4 Å, respectively. These values are much smaller than the typical coordination of a close-packed liquid such as, e.g., l-Mg, indicating some persistence of covalent bonding in l-Bi (see, e.g., Refs. [16,23,24]).

The Bi g_{ie}, as obtained from an average over five configurations, exhibits a prominent peak (see middle panels of Fig. 2). The difference between g_{ie} and $g_{ie,0}$ is in this case less noticeable. In fact, beyond a radius of 1.25 Å g_{diff} (see lower part of Fig. 2) is essentially zero although S_{diff} suggests that there is a nonzero amplitude at a distance of approximately $7.7/2 = 3.85$ Å. Therefore an accumulation of charge in the bonds can be hardly inferred from g_{diff}. There is, however, a significant pileup of charge in between the atoms. This emerges from an analysis of the difference charge density, as done previously for l-Mg. Contours of $n_{diff}(r)$ for a typical l-Bi configuration are plotted in the lower right panel of Fig. 3. This plot shows also large areas of charge depletion close to the atoms. These areas are related to covalent directional bonds having a finite lifetime as found, e.g., in l-Si [24], and cause the spherical average $[\sim g_{diff}(r)]$ around an atom to be almost zero.
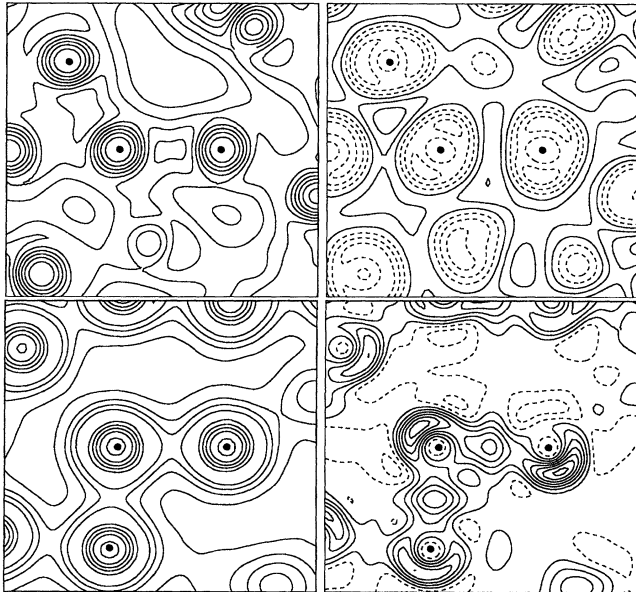

FIG. 2. Contour plots of the pseudocharge density (left) and difference charge density (right) for l-Mg (upper panels) and l-Bi (lower panels). The charge density contours are drawn at densities of $n \times 0.002$ (l-Mg) and $n \times 0.01$ (l-Bi) electrons/(a.u.)^3. Difference charge densities contours (dashed if $n < 0$) are drawn at $n \times 0.001$ electrons/(a.u.)^3. The atoms (black circles) were chosen such that one atom has the other two in the first coordination shell.
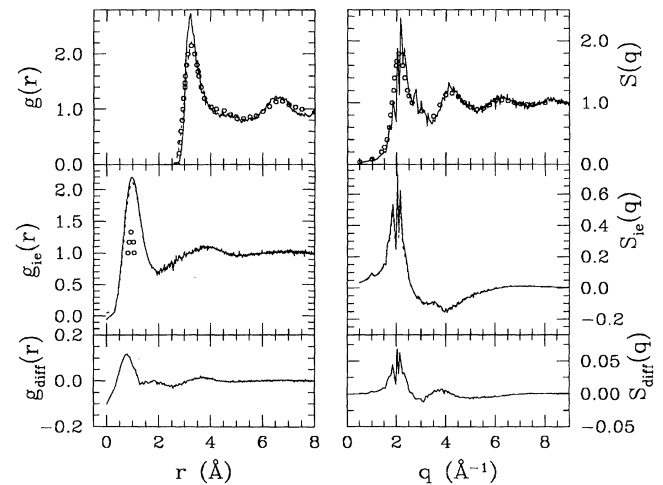

FIG. 3. Bi correlation functions. Top panels show $g(r)$ and $S(q)$. The solid line is the simulation result, the circles pertain to the experiment by Knoll, Lamparter, and Steeb [20] at 923 K. Also the $g(r)$ as obtained by broadening the simulation data with the resolution of Knoll's experiment (12 Å^{-1}) [22] is shown (dotted line). For middle and lower panels, see the caption of Fig. 1. The circles represent the first peak of g_{ie} as determined by Takeda, Tamaki, and Waseda [5].

In Figs. 1 and 2 also some of the experimental points of the g_{ie} as obtained by Takeda and co-workers [5,10] are shown. For l-Bi the position of the peak of our calculated g_{ie} coincides with the position of the first peak of the experimental g_{ie} [5]. However, this is about the only feature that our data have in common with the experimental data that beyond the peak at 1 Å show very strong oscillations. The physical origin of these oscillations cannot be easily understood, and it seems rather likely that they mainly arise from some inaccuracy in the experimental data. Turning now to l-Mg, it appears that, in spite of some evident differences, the overall comparison between theory and experiment [10] is not unreasonable. At variance with our results, the g_{ie} of Takeda and co-workers seems to rise to high values at short distances, but, according to the same authors, their data are not accurate for $r < 0.75$ Å, and also our calculations are in this region not very reliable due to the pseudopotential approximation. Moreover, at larger distances the experiment curiously appears to agree better with the calculated $g_{ie,0}$ than with g_{ie}, which carries the information on the bonding in the liquid. In view of the large experimental error bars, it is difficult to make definite conclusions. More accurate experimental data are clearly necessary for a more quantitative discussion.

In conclusion, on the basis of *ab initio* MD simulations we have presented a detailed analysis of electron-ion pair correlations for l-Mg and l-Bi. We have found that g_{ie} largely reflects the different behavior of the charge density in these two systems, thus allowing one to distinguish a clearly NFE metal like l-Mg from a system with residual covalent bonding effects like l-Bi. However, from our results it also emerges that some care is required in the interpretation of g_{ie}. For systems with an open structure, such as for l-Bi and most likely for l-Si, g_{ie} does not allow it to reveal the occurrence of transient directional bonds, but rather suggests a superposition of atomic charge densities. Instead, g_{ie} provides detailed information on the bonding properties of close-packed systems such as liquid Mg, Na, or Al.

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