Structure and dynamics of liquid Zn: an analysis of ab-initio simulations.

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Abstract. The static and dynamic properties of liquid Zn have been studied using an ab initio molecular dynamics method. Results are reported for the thermodynamic states at 723K near which inelastic neutron and x-ray scattering data are available. The calculated static structure shows very good agreement with experimental measurements, including an asymmetric main peak. The dynamic structure reveals the existence of propagating density fluctuations, and the associated dispersion relation has also been calculated. The possible coupling between longitudinal and transverse excitation modes has been investigated by looking at specific signatures in two wavevector regions: the first one is located around the position of the main peak of the structure factor, q_p , as suggested by the recently reported appearance of high frequency transverse waves in several liquid metals under high pressures; the second region is around $q_p/2$, as suggested by inelastic scattering experiments for liquid Zn and other metals.

1 Introduction.

In the periodic table, zinc is at the end of the transition metals series, presenting a full d shell that contributes in an essential way to its properties. The study of Zn in different states, ranging from small clusters of atoms to the metallic liquid, has shown it to be quite an anomalous system. In small clusters [1] the structure is rather peculiar with a dense core and a separated surface at an expanded distance with respect to the in-core and in-surface interatomic distances. Moreover for some sizes a single atom appears strongly bound to another particular atom via a covalent bond, which coexists with the metallic bonding in the rest of the cluster. When coming to the solid, the ground state is a hexagonal close packed structure, but the ratio between the c and a axis is extremely large, 1.856, around 15 % higher than the ideal value corresponding to hard spheres. Moreover, this value increases with temperature. Such a behaviour is only shared with Cd among single-component solids. The reason lies in an extremely flat energy surface, related to electronic correlation [2]. The liquid structure is also unusual among elemental systems, showing near melting a structure factor with a highly asymmetric main peak [3], a feature only present additionally again in liquid Cd. This asymmetry decreases upon increasing temperature. Finally,

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concerning its dynamic properties, recent measurements performed using either inelastic x-ray scattering (IXS) at 713 K or inelastic neutron scattering (INS) at 773 K, have concluded that the data is compatible with the existence of two types of propagating excitations in the density fluctuations for wavevectors around $q_p/2$, where q_p denotes the position of the main peak of $S(q)$ [4, 5].

These complexities pose therefore the requirement of a highly accurate description of the interactions present in the system in order to carry out a theoretical study of the properties of liquid Zn (l-Zn). Such requirement is certainly met by ab initio molecular dynamics (AIMD) methods based on density functional theory [6]. Curiously, the only study of l-Zn within AIMD simulations [7] considered the orbital-free version of DFT, which, in spite of allowing large simulation samples and long runs, shows some shortcomings, particularly in treating d -band electrons. Here we present the results of a full AIMD study of the properties of l-Zn, in particular its complex dynamics.

2 Computational method.

The simulated sample consists in a set of N bare ions with valence Z , enclosed in a volume V and interacting with $N_e = NZ$ valence electrons. The total potential energy of the system, with ionic positions $\{\vec{R}_I\}$, is written, within the Born-Oppenheimer approximation, as the sum of the direct ion-ion coulombic interaction energy, $E_{i-i}(\{\vec{R}_I\})$, plus the ground state energy of the electronic system subject to the external potential created by the ions, $V_{\text{ext}}(\vec{r}, \{\vec{R}_I\})$,

$$E(\{\vec{R}_I\}) = E_{i-i}(\{\vec{R}_I\}) + E_g[n_g(\vec{r}), V_{\text{ext}}(\vec{r}, \{\vec{R}_I\})] \quad (1)$$

where $n_g(\vec{r})$ is the ground state electronic density. According to DFT, the ground state electronic density minimizes the energy functional

$$E[n(\vec{r})] = T_s[n] + E_{\text{ext}}[n] + E_H[n] + E_{xc}[n] \quad (2)$$

where the terms represent, respectively, the electronic kinetic energy, $T_s[n]$, of a non-interacting system of density $n(\vec{r})$, the classical electrostatic energy (Hartree term), the exchange-correlation energy, $E_{xc}[n]$, for which we have used the generalized gradient approximation [8] and finally the electron-ion interaction energy, $E_{\text{ext}}[n]$.

The ground state density and energy and the forces acting on the atoms are obtained for each ionic configuration, and therefrom the atoms are moved according to Newton's equations of motion, as implemented in the VASP software package [9].

The electron-ion potential has been modeled through an ultrasoft pseudopotential that considers 12 valence electrons, as incorporated in the dataset included in the VASP utility.

3 Results and discussion.

After the 90 Zn atoms, enclosed in a cubic simulation box of side $L = 11.35 \text{ \AA}$, have equilibrated at the desired temperature of 723 K, the system is allowed to evolve for 36000 additional configurations with a timestep of 4 fs, from which the properties of interest are sampled and analyzed.

3.1 Static structure.

The atomic positions are obtained directly from the AIMD run, and the simulation box fixes the wavevectors compatible with the periodic boundary conditions used. Consequently, both the pair distribution function, $g(r)$, and the static structure factor, $S(q)$, can be straightforwardly computed. The results obtained, depicted in figure 1, agree well with all the available experimental measurements, obtained either through neutron diffraction [10], or from x-ray diffraction [3, 11], which are remarkably close to each other. In particular, the asymmetric shape of the main peak of $S(q)$ at $q_p \approx 2.92 \text{ \AA}^{-1}$ is well reproduced in the simulations.

3.2 Dynamic properties

The collective dynamics of density fluctuations in the liquid is described by the intermediate scattering function, $F(q, t)$, which can be computed, for the q vectors allowed by the simulation box, in terms of the time evolution of the particle coordinates.

The dynamic structure factor, $S(q, \omega)$ is the Fourier Transform (FT) into the frequency domain of $F(q, t)$. The scattered intensity obtained in an IXS experiment is directly related to $S(q, \omega)$, although a proper comparison between the AIMD result and IXS data requires taking into account the difference between the simulations, where atoms are classical particles, and the photon scattering which is a quantum process. Therefore the $S(q, \omega)$ is corrected so as to fulfill the detailed balance condition. Moreover the experimental setup is characterized by an energy resolution, which is taken into account through the convolution of the detail-balanced $S(q, \omega)$ with the experimental resolution function. Additionally, IXS intensity is usually given in arbitrary units, and therefore a proper rescaling is needed in the final AIMD vs IXS comparison. Figure 2 shows the results of such comparison for an experimental $q = 1.06 \text{ \AA}^{-1}$, which lies between two values allowed in the simulations. The central peak obtained from AIMD is lower than the experimental data, but the positions of the side-peaks and the general form of the curve are well reproduced. Particularly, in the region between the quasielastic and inelastic peaks both the IXS data and our results show a behavior somewhat different from the expectations based on a simple sum of a diffusive term to account for the central peak and a propagating mode to account for the side peak. This prompted the experimentalists to suggest the existence of a second propagating mode of energy lying within this region, and showed that a fit based on two propagating modes produces better results than a fit based on just one of them. Specifically, they used a Lorentzian function to account for the central peak and a damped harmonic oscillator (DHO) for each of the propagating modes [4]. The variation with q of the frequencies of the modes obtained from the fits leads to a dispersion relation (DR) with two branches, a high frequency one that displays a positive dispersion with respect to the hydrodynamic sound velocity, and that is similar to the usual DR in liquid systems, plus a lower energy branch, which has been interpreted as a fingerprint of transverse waves in the dynamics of density fluctuations. The existence of these two modes was first suggested for liquid Ga and later also for other liquid metals (Sn, Fe, Cu, Na) [4, 13], based on the similarity between the frequencies observed and those of transverse excitations either in the corresponding solid or in the liquid. However, at present no theoretical approach has been able to explain their appearance. The DR observed for l-Zn is shown in the inset of figure 2. INS experiments (although using a different model for fitting) also led to similar conclusions and the corresponding DR is shown in figure 2.

Figure 1. Pair distribution function (up) and static structure factor (down) of l-Zn obtained from AIMD at 723 K (line) compared with several experimental measurements. Circles: x-ray data from Lou *et al* at 710 K [11]; triangles: x-ray data from Waseda at 723 K [3]; squares: neutron data from North *et al* at 723 K [10].

Figure 2. Comparison between AIMD and IXS data for wavevectors (in $\text{\AA}^{-1}$) shown in the legend. Circles: experimental results [4]. Lines: AIMD data (modified for proper comparison with experiment, see text). The encircled region corresponds to the anomalous shape associated to the low energy excitation. The inset shows the dispersion relations for $q < q_p/2$ as obtained from INS (circles) [5], IXS (squares) [4], and AIMD (triangles). The dashed line corresponds to the hydrodynamic sound velocity (2780 m/s) [12].

We have analyzed the $F(q, t)$ obtained in our simulations with models similar to those used by experimentalists, slightly modified to cope with the correct time reversal symmetry of the classical $F(q, t)$. The analytical form used for the diffusive term is given by

$$f^{\text{dif}}(t) = \frac{\alpha}{2} \text{sech}(\beta t). \quad (3)$$

For long times it behaves as a decaying exponential, which is the expected asymptotic behavior for a diffusive term, but for $t = 0$ has null odd derivatives, which is the correct behaviour (contrary to how exponentials behave at $t = 0$).

The DHO model corresponds to a sum of two complex-conjugate exponential functions, subject to the condition of null first derivative at $t = 0$. It reads

$$f^{\text{DHO}}(t) = A \exp[-\gamma t] \left(\cos(\omega_o t) + \frac{\gamma}{\omega_o} \sin(\omega_o t) \right). \quad (4)$$

This is exactly the form in which a damped harmonic oscillator oscillates for initial position given by A and null initial velocity. It is however important to remember that the oscillation frequency ω_o is not the natural frequency of the oscillator, since it is affected by the damping coefficient γ . The natural frequency is in fact $\Omega_+ = \sqrt{\omega_o^2 + \gamma^2}$. This is therefore the characteristic frequency, or what we call the mode frequency. It is also interesting to consider the quantity $\Omega_- = \sqrt{\omega_o^2 - \gamma^2}$. The reason is that the FT of $f^{\text{DHO}}(t)$, namely $\tilde{f}^{\text{DHO}}(\omega)$, shows a peak at Ω_- whenever this magnitude is real, i.e. if $\gamma < \omega_o$. Additionally it should be noted that $\omega^2 \tilde{f}^{\text{DHO}}(\omega)$ always has a peak, located at Ω_+ .

Summarizing, by fitting $F(q, t)$ to a sum of a diffusive term and two DHOs we are obtaining the damping coefficients (γ) and the oscillation frequencies corresponding to the two propagating modes (ω_o), and from them we can construct the frequencies where in absence of other terms the dynamic structure factor would show a peak (Ω_-) and the mode frequencies (Ω_+) which coincide with the frequencies where the longitudinal current spectrum (see below) would show a peak in absence of other terms. In fact one should remember that the presence of other terms (the diffusive one and the other propagating mode) will in general modify the positions of the peaks, or may even make them disappear turning them into shoulders or masking them completely if the amplitude is small.

For completeness we mention that in experiments the fit is performed for $S(q, \omega)$ and the parameter obtained from the fit is directly Ω_+ .

Coming to the results, we again obtain a better fit to the AIMD calculated $F(q, t)$ when 2 DHOs are used, and their corresponding frequencies are displayed in figure 2. Our data are more in line with the IXS results, but in any case support the existence of two propagating modes in this wavevector region.

We have extended the analysis to higher wavevectors, where $F(q, t)$ starts being dominated by strong structural relaxations that ultimately lead to the de Gennes slowing down near q_p , by looking at the current correlation functions. We want to study the possible existence of two propagating modes in the longitudinal current correlation functions, whose FT, $C_L(q, \omega)$, is directly related to the dynamic structure factor, since $C_L(q, \omega) = \omega^2 S(q, \omega)/q^2$ [note that $C_L(q, \omega = 0)$ must therefore be zero]. This relation is a consequence of the continuity equation relating density and current, which in the time domain means that $C_L(q, t) = -(d^2 F(q, t)/dt^2)/q^2$. Also the spectra of the transverse current correlation functions, $C_T(q, \omega)$, were analyzed in order to compare with the characteristic frequencies that appear in the longitudinal currents. The transverse current does not fulfill a continuity equation, so $C_T(q, \omega = 0)$ can have any non-zero value.

The longitudinal spectra always shows one maximum, whose frequency, $\omega_L(q)$, determines the DR of the longitudinal peaks, shown in figure 3. Even so, the evolution of $\omega_L(q)$ with q displays a quite abrupt change around $q \approx 2 \text{ \AA}^{-1}$, and also around $q \approx 3.4 \text{ \AA}^{-1}$. This suggests the existence of two modes of varying amplitude rather than the rapid variation of the frequency of a single mode. This possibility is further analyzed below. The transverse spectra, on the other hand, behaves in a peculiar way, since in the q -region around q_p two maxima appear. The low energy peak has the usual behaviour for liquids: it first appears at a non-zero value of q , where shear waves start being supported, and then shows a quite small dispersion until eventually the peak returns to zero frequency in the single particle regime of large q . The appearance of the second high frequency peak in $C_T(q, \omega)$ had indeed been observed before, but only for liquids under high pressure [14], so it is rather surprising to find them at ambient pressure as we do here. However, we note that this behaviour is also observed in other metals at ambient pressure, such as liquid Ni [15].

The double peak structure of $C_T(q, \omega)$ near q_p as well as the rapid variation of $\omega_L(q)$ in the two regions mentioned above suggest the existence of two propagating modes both in the longitudinal and in the transverse current correlation functions for $q > q_p/2$. In order to analyze this possibility we have performed fits based on the DHO model for both functions.

The models used for the fits of the longitudinal and transverse currents must be different for the reasons commented above. In order to be consistent with the fit of $F(q, t)$, the model used in the case of $C_L(q, t)$ includes the second derivative of

Figure 3. DR of the peaks in the longitudinal (circles) and transverse (squares) spectra.

Figure 4. DR of the DHO modes found from the fits to the longitudinal (triangles) and transverse (diamonds) current correlation functions.

the diffusive model used for $F(q, t)$ and two functions that correspond to the second derivative of the DHO model. In the case of $C_T(q, \omega)$ we have found that two DHOs provide a good fit to the calculated functions above approximately $q_p/2$, but for lower q one DHO plus one diffusive mode represents better the data.

The DR of the DHO mode frequencies is shown in figure 4. We want to remark three points regarding the comparison between figures 3 and 4. First, the observed “jumps” in $\omega_L(q)$ in fact correspond to transitions from one of the longitudinal modes to the other, with the amplitude of one mode decreasing and the amplitude of the other mode increasing. Second, there is a large difference between the position of the peaks in $C_T(q, \omega)$, shown in figure 3, and the mode frequencies, shown in figure 4. This is due to the large damping coefficients of the transverse modes, that makes Ω_- (which is near the position of the peak) rather smaller than Ω_+ . Finally, we observe that the low frequency longitudinal mode has a numerical value, for $q < 2 \text{ \AA}^{-1}$, very close to the frequency of the transverse mode when only one is present, or to the low frequency transverse mode when there are two. This fact suggests, once more, that the weak low frequency excitations observed in the dynamic structure factor or in the longitudinal current spectra are somehow related to the transverse waves that propagate in the liquid in this range of q .

4 Conclusions.

We have performed the first full AIMD study of the complex dynamics of liquid Zn, recovering the main characteristics of the experimental data, and analyzed the results obtained through the use of models similar to those used experimentally. The analysis unveils the existence of two propagating modes for the longitudinal and the transverse waves, leading near the position of the main peak to two peaks in the transverse current spectra, a feature previously observed only for high pressures. Finally the numerical similarity between the frequencies obtained in the region $q < 2 \text{ \AA}^{-1}$ suggests a transverse-like character of the low energy excitations observed in the dynamic structure factor. Nevertheless there is a clear call for a theoretical analysis that clarifies which mechanisms render this possible.

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