Dynamic Structure in a Molten Binary Alloy by ab-initio Molecular Dynamics: Crossover from Hydrodynamics to the Microscopic Regime.

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The dynamic structure factor of the $^{7}\text{Li}_{0.61}\text{Na}_{0.39}$ liquid alloy at $T = 590$ K has been calculated by ab initio molecular dynamics simulations using 2000 particles. For small wavevectors, $0.15 \leq q/\text{Å}^{-1} \leq 1.6$, we find clear side peaks in the partial dynamic structure factors. Whereas for $q \leq 0.25$ $\text{Å}^{-1}$ the peak frequencies correspond to the hydrodynamic sound dispersion of the binary alloy, for greater $q$-values we obtain two modes with phase velocities above and below the hydrodynamic sound. A smooth transition between hydrodynamic sound and the two collective modes is shown to take place in the range $0.25 \leq q/\text{Å}^{-1} \leq 0.35$. The mass ratio in this system, $m_{\text{Na}}/m_{\text{Li}} \approx 3$, is the smallest one so far for which the fast mode is observed. We also predict that inelastic X-ray scattering experiments would be able to detect the slow mode, and explain why the inelastic neutron scattering measurements [P.R. Gartrell-Mills et al, Physica B 154, 1 (1988)] do not show any of these modes.

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Interest in the collective excitations in liquid binary mixtures was generated by the pioneering molecular dynamics (MD) study on the dynamics of the liquid Na-K alloy \cite{1}. It was further stimulated by the MD results for liquid Li$_4$Pb, where a new, high-frequency mode, supported by the light Li atoms only (the so-called “fast sound”) was identified \cite{2}. Kinetic theory calculations \cite{3} for two-component fluids with large atomic mass difference, confirmed the appearance of a collective mode at high frequencies, $\omega$, and wave numbers $q \geq q_h$, where $q_h$ denotes the upper limit of the hydrodynamic regime. Moreover, this mode propagated with a phase velocity close to that of the pure light component, which was clearly greater than the hydrodynamic sound velocity, $c_h$, of the two-component system. Subsequently, calculations based on the revised Enskog theory for binary mixtures of hard spheres with a large mass difference \cite{4} predicted two propagating collective modes in addition to hydrodynamic sound. One of these was identified with the fast sound while the other mode, which had propagating phase velocities below $c_h$, was consequently termed “slow sound”. Theoretical \cite{4,5,6}, computer simulation \cite{7,8,9,10} and experimental \cite{11,12,13,14,15} studies have investigated the existence and properties of these collective modes. Experimental evidence for the fast sound has been obtained for systems such as H$_2$-Ar, H$_2$-Xe and He-Xe mixtures by light scattering \cite{15}, and He-Ne, He-Ar and Li$_4$Pb by inelastic neutron scattering (INS) \cite{15,16,17}. Note that all these systems except Li$_4$Pb are gas mixtures, whereas the latter is pseudoionic mixture, and that the mass ratio varies from around 33 for He-Xe to around 5 for He-Ne.

There has been discussion concerning the way in which the two collective modes connect with the hydrodynamic one when $q_h$ is approached from above. Some theoretical and MD results for He-Ar and He-Ne mixtures have suggested that either the fast and slow sound merge into the hydrodynamic sound \cite{18}, or that the fast sound disappears at $q_h$, and the slow sound merges into the hydrodynamic one, with a predicted value \cite{19,20,21} for $q_h \approx 0.07$ $\text{Å}^{-1}$. A similar value for $q_h$ has recently been obtained for liquid Li$_4$Pb by both INS and by MD calculations \cite{22,23,24}. Recent MD calculations \cite{25,26}, which followed the INS measurements of Bafle et al \cite{27}, for the dynamic structure of a He$_{0.77}$Ne$_{0.23}$ gas mixture at two densities, showed a clear crossover from hydrodynamics to fast and slow modes at $0.2 \leq q/\text{Å}^{-1} \leq 0.5$. Moreover, $q_h \approx 0.2$, which is substantially greater than previous estimates.

The present communication addresses the previous questions while providing further insight into the microscopic dynamics of the Li$_{0.61}$Na$_{0.39}$ liquid alloy. This is a metallic system, with a rather small mass ratio $\approx 3$, to which much theoretical and experimental attention has been devoted because of its strong phase separating tendencies. It has a consolute point at $T \approx 577$ K and concentration $c_{\text{Li}} \approx 0.64$, close to the “zero alloy” composition ($c_{\text{Li}} \approx 0.61$) for which the total static structure factor, $S(q)$, reduces to the concentration partial structure factor $S_{\text{CC}}(q)$, i.e., $S(q) = S_{\text{CC}}(q)/c_{\text{Li}}c_{\text{Na}}$, because of the negative scattering length of the isotope $^7\text{Li}$. The $S(q)$ has been measured at several temperatures and concentrations \cite{27}, and INS measurements \cite{28} have been performed for several temperatures at the zero alloy composition. The measured total dynamic structure factor, $S(q,\omega)$, in the explored $(q,\omega)$ region decreased monotonically as a function of $\omega$, and side peaks, which would have been indicative of collective modes, were absent.

The present study has used the orbital-free ab initio molecular dynamics (OF-AIMD) method, where the forces acting on the nuclei are computed from electronic structure calculations, based on density functional theory (DFT), which are performed as the MD trajectory is gen-
erated. A simple liquid metallic alloy, $A_xB_{1-x}$, is treated as a disordered array of bare ions interacting with the valence electrons through electron-ion potentials. The total potential energy of the system can be written, within the Born-Oppenheimer approximation, as the sum of the direct ion-ion coulombic interaction energy and the ground state energy of the electronic system, $E_0[p_0(r)]$. According to DFT, the ground state electronic density, $\rho(r)$, minimizes an energy functional which is given as the sum of the kinetic energy of independent electrons, $T_k[p]$, the classical Hartree electrostatic energy, $E_H[p]$, the exchange-correlation energy, $E_{xc}[p]$, for which we have adopted the local density approximation and finally, the electron-ion interaction energy, $E_{ion}[\rho]$ for which we have used local ionic pseudopotentials constructed within DFT [18]. In the OF-AIMD approach [19 20] an explicit but approximate functional of the density is used for $T_k[p]$. Proposed functionals consist of the von Weizsäcker term, $T_W[p(r)] = \frac{1}{2} \int d\vec{r} |\nabla \rho(r)|^2/\rho(r)$, plus further terms chosen in order to reproduce correctly some exactly known limits. Here, we have used a simplified version of the average density models, developed by García-González et al [21] in which $T_\alpha = T_W + T_\beta$, where

$$T_\beta = \frac{3}{10} \int d\vec{r} \rho(r)^{5/3-2\beta} \tilde{k}(\vec{r})^2$$

$$\tilde{k}(\vec{r}) = (3\pi^2)^{1/3} \rho(\vec{r})^{5/3}$$

$k(\vec{r}) = (3\pi^2)^{1/3} \rho(\vec{r})^{5/3}$, $k_\rho$ is the Fermi wavevector for mean electron density $\rho_0$, and $w_\beta(x)$ is a weight function chosen so that both the linear response theory and the Thomas-Fermi limits are correctly recovered. Further details of this functional are given in reference [18] and we merely note that in the present simulations we have used $\beta = 0.51$.

We have performed OF-AIMD simulations for the Li$_{0.61}$Na$_{0.39}$ liquid alloy at temperature $T = 590K$ and number density $\rho = 0.03218 \text{ Å}^{-3}$. The cubic simulation box contained 2000 particles. Given the ionic positions at time $t$, the electronic density is expanded in plane waves, and the energy functional is minimized with respect to the plane wave coefficients yielding the ground state electronic density and energy. The Hellmann-Feynman theorem is used to obtain the forces on the ions which, along with the Verlet leapfrog algorithm, are used to update the ionic positions and velocities. The timestep was 0.0025 ps, the equilibration lasted for 10 ps and the calculation of properties was made averaging over another 60 ps. The cutoff energy for the plane wave expansion was 8.15 Ryd, giving a basis of about 85000 plane waves. These choices allow a minimum $q$-value of 0.158 Å$^{-1}$ which will permit investigation of length and time scales covering a range which includes the hydrodynamic regime.

The total dynamic structure factor $S_T(q, \omega)$, which is directly related to the intensity obtained in either an inelastic neutron (INS) or X-ray scattering (IXS) experiment, is a weighted average of the partials $S_{ij}(q, \omega)$, defined as

$$S_{ij}(q, \omega) = \frac{1}{2\pi (N_i N_j)^{1/2}} \int dt \ e^{i\omega t} \langle \rho_i(\vec{q}, t) \cdot \rho^*_j(\vec{q}, 0) \rangle$$

(2)

where $N_i$ is the number of $i$-type particles, the $\langle \ldots \rangle$ stands for the ensemble average, the asterisk denotes complex conjugation, $\rho_i(\vec{q}, t) = \sum_{i(j)=1}^{N_i} \exp[i\vec{q} \cdot \vec{R}(j)(t)]$ represents the density fluctuations of the $i$-th component with wavevector $\vec{q}$, and $\vec{R}(j)(t)$ is the position of the $i$-type particle $j$ at time $t$. The $S_T(q, \omega)$ observed in an IXS experiment is given by

$$S_T^{(INS)}(q, \omega) = \sum_{i,j=1}^{2} (c_i c_j)^{1/2} \frac{f_i(q) f_j(q)}{(f^2(q))} S_{ij}(q, \omega)$$

(3)

where $f_i(q)$ are the atomic scattering factors and $(f^2(q)) = \sum_{i=1}^{c_i} f_i^2(q)$. Correspondingly, in an INS experiment

$$\langle b^2 \rangle S_T^{(INS)}(q, \omega) = \sum_{i=1}^{c_i} (b_i^2) - \langle b_i \rangle^2 c_i S_i^*(q, \omega)$$

$$+ \sum_{i,j=1}^{c_i c_j} (c_i c_j)^{1/2} \langle b_i \rangle \langle b_j \rangle S_{ij}(q, \omega)$$

(4)

where the $S_i^*(q, \omega)$ are the self-dynamic structure factors, $\langle b_i \rangle$ is the coherent scattering length, $4\pi \langle b^2_i \rangle$ is the total scattering cross section and $\langle b^2 \rangle = \sum_{i=1}^{c_i} c_i \langle b^2_i \rangle$ is the average cross section per atom.

The results for $S_{LiLi}(q, \omega)$ and $S_{NaNa}(q, \omega)$ are shown in fig. 3 for three representative $q$-values. At the smallest $q$-value allowed by the simulations, $q = 0.158 \text{ Å}^{-1}$, both $S_{LiLi}(q, \omega)$ and $S_{NaNa}(q, \omega)$ show clear Brillouin peaks at a common frequency, $\omega_B$, which is the typical behaviour in the hydrodynamic region and indicates a propagating sound mode with a hydrodynamic velocity $c_h = \omega_B/q \approx 3000 \text{ m/s}$. $S_{LiLi}(q, \omega)$ exhibits Brillouin peaks for the other two $q$-values of fig. 3 and continues to show side peaks or shoulders up to $q \approx 1.5 \text{ Å}^{-1}$, whereas $S_{NaNa}(q, \omega)$ has only a shoulder for $q = 0.48 \text{ Å}^{-1}$ and this feature disappears at $q \approx 0.9 \text{ Å}^{-1}$. In contrast, the partial longitudinal currents, $C_{ij}(q, \omega) = \omega^2 S_{ij}(q, \omega)$, show clear peaks at any $q$-value. At the lowest $q$-value, the frequencies of the maxima in the $C_{ij}(q, \omega)$ coincide with those of the Brillouin peaks, but at larger $q$ they are somewhat higher because of the contribution from the damping terms [3]. Moreover, as $q$ increases $C_{12}(q, \omega)$ diminishes pointing to a progressive decoupling of the motions of two species.

The dispersion curves $\omega_{LiLi}(q)$ and $\omega_{NaNa}(q)$ of the inelastic peaks in $S_{LiLi}(q, \omega)$ and $S_{NaNa}(q, \omega)$ respectively,
exhibits a peak at a frequency between that of Si. Fig. 3 the partials under understanding of this anomaly we have also plotted in apperance of collective modes in the simulation. For an S with no side peaks as a function of the INS measurements [17] gave a total structure factor tion of these collective modes. As already mentioned, Sics begins already at branching suggests that the departure from hydrodynam- than in fig. 2. The frequencies for both Li and Na are larger in the alloy. The fast mode involves the Li decoupling of the species, and giving rise to fast and slow sound modes in the alloy. The fast mode involves the Li ω ≈ 0.3 Å⁻¹, ω LiLi(q) and ω NaNa(q) show the same linear behaviour of hydrodynamic collective excitations propagating with speed cₙ ≈ 3000 m/s. Above this q-value, the dispersion curve splits into two branches signalling the onset of dynamic decoupling of the species, and giving rise to fast and slow sound modes in the alloy. The fast mode involves the Li particles only, with a phase velocity cₙ = ω LiLi(q) /q ≈ 3800 m/s, whereas the slow mode phase velocity is cₛ = ω NaNa(q) /q ≈ 2100 m/s, at q ~ 0.65 Å⁻¹. We have also performed OF-AIMD simulations for pure Li at the same temperature and total number density as the alloy, and the calculated sound velocity, 3900 m/s, is very close to the velocity of the fast mode. Following usual prac- tice [1], we have also obtained dispersion curves derived from the maxima in Cij(q, ω), and these are also shown in fig. 2. The frequencies for both Li and Na are larger than ω LiLi(q) and ω NaNa(q), and the earlier onset of the branching suggests that the departure from hydrodynamics begins already at q ~ 0.15 Å⁻¹. Moreover, the higher slope obtained for the Li leads to a larger estimation for the phase velocity of the fast mode (cₙ ≈ 4600 m/s).

Now we consider the possible experimental observation of these collective modes. As already mentioned, the INS measurements [17] gave a total structure factor with no side peaks as a function of ω. We have calculated S(INS) T(q, ω) using eqn. (4) and data from our simulations. The results illustrated in fig. 3 do not show side peaks in agreement with the experiment, and despite the appearance of collective modes in the simulation. For an understanding of this anomaly we have also plotted in fig. 3 the partials Sij(q, ω). We see that S(INS) T(q, ω) also exhibits a peak at a frequency between that of S LiLi(q, ω) and S NaNa(q, ω). In the weighted average of eqn. (4), the negative scattering length of the ⁷Li isotope (|b₇Li| = 0.22 × 10⁻¹² cm) gives rise to a negative contribution from the partial S NaNa(q, ω) which balances the contributions from the peaks in S LiLi(q, ω) and S NaNa(q, ω). In contrast, we predict that side peaks would be observed in an IXS measurement because the atomic form factors involved in the average in eqn. (4) always take positive values. Moreover, the peaks would be those due to the slow sound because the prefactor of S NaNa(q, ω) is about twenty times larger than that of S LiLi(q, ω) and twice that of S LiLi(q, ω), with the overall result that the the total S (INS) T(q, ω) is mainly controlled by S NaNa(q, ω).

In conclusion, our simulations of the Li₀.₆₁Na₀.₃₉ liquid alloy show well defined collective modes analogous to those already found in other binary fluids. However, this system has the smallest mass ratio considered so far and is the first metallic system for which “fast sound” appears. The results for the INS total dynamic structure factor explain the reason for the failure to detect collective excitations in the INS experiment by Gartrell-Mills et al [17]. However, we predict that these excitations, particularly the slow sound mode, would be observed in an IXS experiment.

In order to specify where the transition from hydrodynamics to kinetic regime takes place, we have found that it is important to specify which magnitude is used. In particular, partial currents depart from hydrodynamic behavior for smaller q-values than the corresponding partial structure factors, and this must be taken into account.
in discussions of the onset of “fast sound”.

Finally, we have shown that it is now possible to perform *ab-initio* molecular dynamics simulations to study the dynamic properties of fluids. The OF-AIMD method, which employs the electron density as the basic variable, gives an approximate treatment of the electron kinetic energy, but within this limitation allows the simulation of large samples for long runs. These are basic requirements for performing reliably the ensemble averages that define most dynamic properties in liquids, as well as for studying the ordering tendencies in multicomponent systems.

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