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Quasi-bound atoms in collective dynamics of liquid Sb

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Abstract

We report an *ab initio* simulation and theoretical study of collective dynamics in liquid Sb at 973 K. An application of the GCM (generalized collective modes) theoretical approach to analysis of simulation-derived time correlation functions resulted in two types of propagating eigenmodes. We found that the almost flat dispersion of the high-frequency branch of propagating modes can be explained by out-of-phase oscillations of nearest neighbors which form quasi-bound atomic pairs for at least 30 ps. We discuss the features of collective dynamics in non-simple metallic melts containing quasi-bound pairs.

INTRODUCTION

Collective dynamics in liquids has specific features defined by two mechanisms of sound propagation: on macroscopic distances due to local conservation laws and on nanoscales due to regular elastic forces. That is why usually the propagation of longitudinal acoustic modes is characterized on different spatial scales by two different quantities: adiabatic speed of sound c_s and high-frequency (elastic) speed c_∞. For comparison, in transverse case the existence of the only conserved transverse quantity, the transverse component of total momentum, excludes a possibility to obtain from its balance a second order differential wave-type equation, that results in the absence of the macroscopic transverse sound in liquids, while in elastic regime (outside the hydrodynamic region) the overdamped shear waves can exist [1–3].

Upon getting outside the hydrodynamic region the most obvious non-hydrodynamic effects are a deviation from the linear hydrodynamic acoustic dispersion law $\omega_s(k) = c_s k$, where ω_s and k are the frequency and wave number, and emergence of shear waves in transverse case. The deviation of the longitudinal dispersion law outside the hydrodynamic regime can be either ”positive” towards higher frequencies as it is typical for dense liquids or ”negative” due to strong effect of damping from a coupling to thermal fluctuations [4]. For liquids which cannot be called as simple ones there exist new features in dispersion law of longitudinal modes, observed in scattering experiments and molecular dynamics (MD) simulations, and which are under active debates. The scattering experiments on liquid Bi [5, 6] and liquid Sb [6] as well as *ab initio* simulations of these liquid metals [6, 7] revealed that the dispersion in the region of the first pseudo-Brillouin zone $k_p/2$ (where k_p is the location of the main peak of static structure factor $S(k)$, does not have the simple form with a maximum at $k_p/2$ but shows quite an extended plateau [5, 6]. The origin of the extended high-frequency plateau in dispersion of longitudinal propagating modes in liquid Bi and Sb so far remains unclear. Both liquid metals show ability to form short-time chemical bonds which lead to a possible emergence of dimers, trimers and more sophisticated short-time complexes [7].

From the point of view of collective dynamics the existence of short-time living complexes can be treated as a dynamics of chemically reacting mixtures. The theory of long-wavelength dynamics for such systems was developed in Refs.[8–10], and the main effect on dynamics in the long-wavelength region was found to be the existence of relaxation processes due to mutual diffusivity of atomic and quasi-bound species, that causes the difference with relaxation behaviour of simple one-component liquid. From the other point of view an atomic pair confined by a chemical bond must have the normal modes with opposite phases of motion for bound particles, as well as to perform some rotational moves. There is a need to develop models within generalized hydrodynamics which can account for existence of the quasi-bound complexes in liquids. With this in mind we will study the collective dynamics of liquid Sb with a focus of defining the quasi-bound pairs of atoms and how they can be treated in generalized hydrodynamic schemes.

The remaining part of this paper is organized as follows: in the next section we provide information about our *ab initio* simulations of liquid Sb. In Section III we will use the five-variable thermo-viscoelastic dynamic model for analysis of dynamic eigenmodes in liquid Sb. Then we will check out the most living quasi-bound pairs (QBP) of atoms, which will be used for defining a corresponding dynamic variable, and which will be used for estimation of related time correlation functions and spectra of "bare" collective modes. We will summarize the conclusions of this study inthe last section.

AB INITIO MOLECULAR DYNAMICS SIMULATIONS

We simulated liquid Sb at 973 K using a system of 600 particles in NVT ensemble by VASP package[11–13]. The electron-ion interaction was represented by PAW potentials[14, 15] with five valence electrons. The PAW potentials have an essentiav advantage over the standard pseudopotentials because they allow to recover the correct nodal structure of wave functions in core region. The plane-wave cut-off energy was 215.05 eV (which is a default one for "precision high" tag in VASP), and only Γ point was used in sampling of the 1800 electronic states in Brillouin zone. The generaized gradient approximation in Perdew-Burke-Ernzerhof formulation[16] was applied for exchange-correlation effects in the electron density functional. The time step in simulations was 3 fs, and upon an equilibration over 8 ps the production run of 54 ps was used to obtain trajectories of particles, their velocities along the trajectories and correcponding forces acting on partiales. All these quantities were used to sample spatial Fourier components of dynamic variables of particle density $n(k,t)$, density of total momentum $\mathbf{J}(k,t)$ and first time derivatives of the total momentum, which is directly connected to the longitudinal (L) and transverse (T) components of the stress tensor via

$$\dot{J}^{L/T}(k,t) \equiv \frac{dJ^{L/T}(k,t)}{dt} = ik\sigma^{L/T}(k,t) \; .$$

These dynamic variables along with the spatial Fourier components of energy density $\varepsilon(k,t)$ and energy current $\dot{\varepsilon}(k,t)$ form the set of dynamic variables of the thermo-viscoelastic (TVE) description of the collective dynamics in liquids[2, 4]

$$\mathbf{A}^{(TVE)}(k,t) = \left\{ n(k,t), J^L(k,t), \varepsilon(k,t), \dot{J}^L(k,t), \dot{\varepsilon}(k,t) \right\} . \tag{1}$$

Analytical solutions for the long-wavelength asymptotes of longitudinal collective modes within the TVE dynamic model were given in [4]. In order to obtain k-dependent propagating and relaxing collective modes in a wide range of wavenumbers one has to solve the eigenvalue problem for a generalized hydrodynamic matrix $\mathbf{T}(k)$ obtained for a chosen set of N_v dynamic variables from the generalized Langevin equation[17]. In this study the TVE set of dynamic variables was used to generate the matrix $\mathbf{T}(k)$ and solve the eigenvalue problem using as an input the correlators from AIMD like it was proposed in [18, 19].

RESULTS AND DISCUSSION

The standard information about microscopic atomic structure of liquids can be obtained from pair distribution function $g(r)$ and static structure factor $S(k)$. The pair distribution function for the simulated liquid Sb has its first peak at the distance 3.05Å corresponding to the most probable distance to the nearest neighbors, and a well-defined shoulder at $r \sim 4-5$Å, which makes evidence of another preferred location of the nearest neighbors. Note, that a splitting of the first coordination shell with a pressure increase was observed even in liquid Li and was caused by strong redistribution of electron density at high pressures [20, 21]. The static structure factor, calculated via instantaneous density-density correlations $S(k) = \langle n(-k)n(k) \rangle$ is shown in Fig.1b. For our study it is important that the main peak of structure factor is located at $k_p \approx 2.15$Å^{-1}, and hence, the first pseudo-Brillouin zone should have its boundary at $k_p/2 \sim 1.07$Å^{-1}.

The single-partricle dynamics in liquids usually is represented by mean square displacements (MSD) $\langle \delta R^2(t) \rangle$ and velocity autocorrelation function (VACF) $\psi(t) = \langle \mathbf{v}_i(t)\mathbf{v}_i(0) \rangle$, where both time-dependent functions were averaged over all particles and different origins

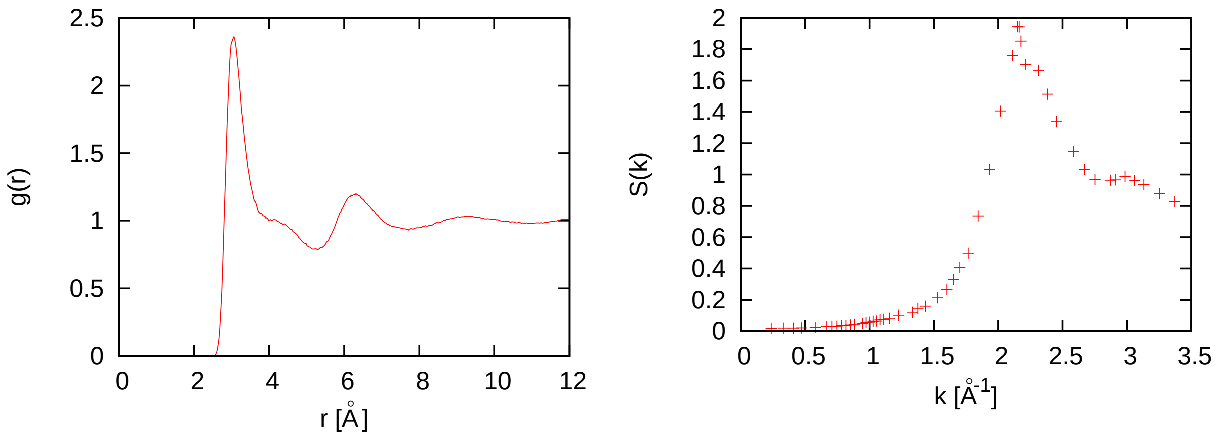

FIG. 1: Pair distribution function $g(r)$ and static structure factor $S(k)$ of liquid Sb at T=973K from *ab initio* simulations.

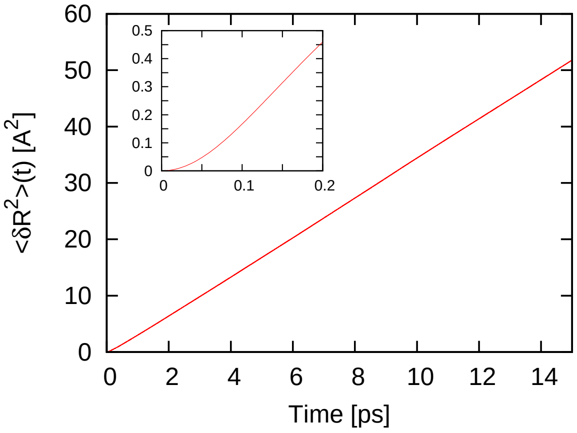

FIG. 2: Mean square displacements of Sb atoms with linear long-time behavior corresponding to difusion constant of 0.583 Å^2/ps. The inset shows the correct ballictic short-time regime of the mean square displacements $\sim t^2$.

of the time correlations. The MSD has typical behavior at small and large times: ballistic regime $\sim t^2$ (see inset in Fig.2) is replaced by the diffusive one which is perfectly linear at large time (Fig.2) resulting in the diffusion coefficient $D = 0.583 Å^2/ps$.

The Kubo-Green integration of the VACF resulted in the same value of diffusion coefficient within the error bars of 3% as estimated from MSD. Another very important quantity obtained from VACF is its frequency spectrum, which outside the low-frequency region (dominated by diffusive contribution to VACF) can reflect the vibrational density of states. In Fig.3 one can see a well-defined maximum in the region of frequencies $\omega \sim 18ps^{-1}$ which

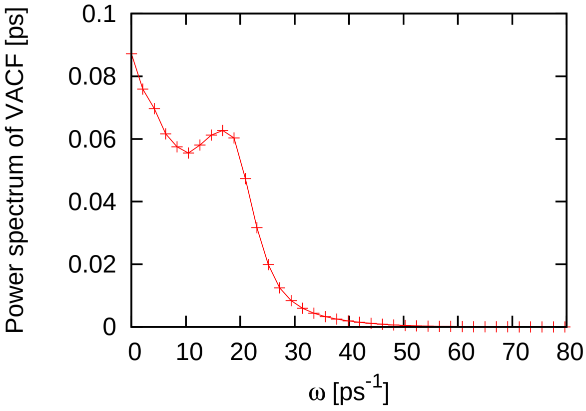

FIG. 3: Power spectrum of velocity autocorrelation function. The high-frequency region corresponds to the vibrational density of states with a peak at $\sim 18\text{ps}^{-1}$.

typically should correspond either to the maximum in dispersion of collective modes at the boundary of the pseudo-Brillouin zone (Debye-like frequency) or to a flat region of the dispersion curve.

For estimation of dispersion of collective excitations in liquid Sb we made use of two approaches. The standard one is for purely numerical estimation of dispersion of extended acoustic modes $\omega_L(k)$ via peak positions of the longitudinal current spectral functions $C^L(k,\omega)$, defined as

$$C^{L/T}(k,\omega) = \frac{1}{mk_BT}\int_0^\infty F_{JJ}^{L/T}(k,t)dt \ . \qquad (2)$$

The second approach is a combination of theory and simulations, the GCM approach, which allows to analyze the shape of time-dependent correlations via contributions from dynamic relaxing and propagating eigenmodes. In this study we made use of the thermo-viscoelastic model[4, 18] of generalized hydrodynamics which accounts for stress fluctuations and heat current fluctuations in addition to standard fluctuations of conserved quantities. It is important that the GCM approach within the thermo-viscoelastic model explicitly fullfills the standard sum rules for the short-time behavior of density-density correlations up to the fourth frequency moment of dynamic structure factor. In Fig.4 we show how the thermo-viscoelastoc model of generalized hydrodynamics recovers the shape of AIMD-derived density-density and longitudinal current-current time correlation functions for different wave numbers. Within

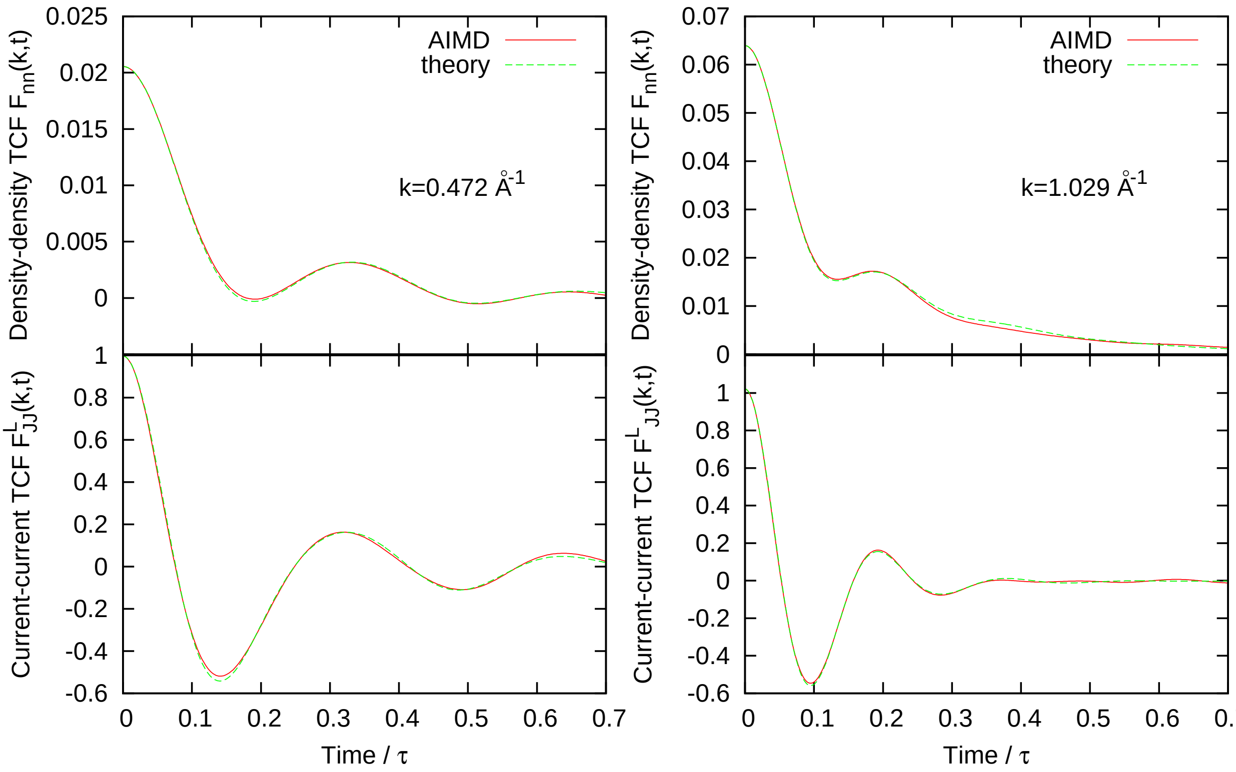

FIG. 4: Density-density and longitudinal current-current time correlation functions at two wave numbers obtained from AIMD simulations (solid red lines) and from the thermo-viscoelastic dynamic model of GCM theory (dash green lines).

the N_v-variable GCM theory the time correlation functions are represented as

$$F_{ij}(k,t) = \sum_{\alpha=1}^{N_v} G_{ij}(k) e^{-z_\alpha(k)t} \ , \tag{3}$$

where $z_\alpha(k)$ is the α-th real (relaxing mode) or complex (propagating) eigenmode, and complex in general weight coefficients $G_{ij}(k)$, which are directly related to the eigenvectors of the α-th collective mode [17]. Similar exponential expansions for time correlation functions were used in [22, 23]

The frequencies of propagating eigenmodes of the thermo-viscoelastic model for liquid Sb are shown in Fig.5 by cross and star symbols. For comparison a dispersion estimated via the peak positions of the current spectral function $C^L(k,\omega)$ at different k-values sampled in AIMD is shown by plus symbols with error bars. In general, the AIMD-derived dispersion is very similar as obtained from IXS experiments on liquid Sb at 973 K[6] and from *ab initio* simulations [7]. The very striking feature of this numerically estimated dispersion is in a

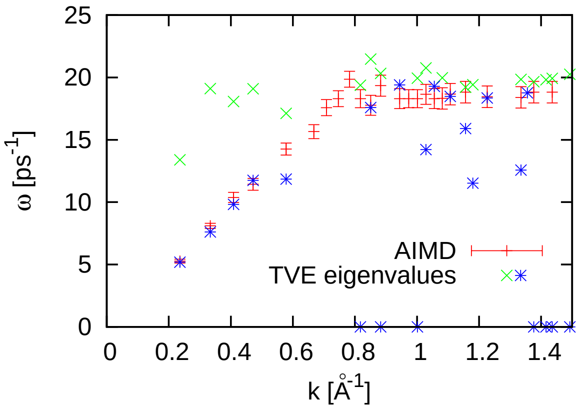

FIG. 5: Dispersions of two branches of propagating eigenmodes from the 5-variable GCM theory (1) in comparison with the dispersion of collective excitations obtained directly from AIMD via peak positions of the current spectral function (2). Existence of a nonacoustic branch of high-frequency propagating modes (green cross symbols) right in the region of a peak in power spectrum of VACF (Fig.3) follows from the GCM theory.

quite extended flat region in wave numbers at the frequency $\sim 18ps^{-1}$, which practically coincides with the high-frequency peak location in the frequency spectrum of VACF (Fig.3). Surprisingly, for one of the two propagating GCM eigenmodes the region of wave numbers at the frequency $\sim 18-20ps^{-1}$ is much more extended and starts at $k \sim 0.3\text{Å}^{-1}$, while in this region and for smaller wave numbers the low-frequency branch shows typical increasing with k behavior of the dispersion of acoustic modes. To some extent the behavior of the dispersion of high-frequency eigenmodes resembles the optic branch in binary liquids[24, 25].

In order to explain the high-freuqency eigenmodes in Fig.5 we checked the time evolution of distances between all the pairs of particles in our simulations, selecting among them those which remain the nearest neighbors for time at least 30 ps. We have chosen a cut-off distance of 5Å in order to include the region of the first maximum and shoulder in Fig.1a. We allowed the particles for not more than 100 timesteps to cross the sharp cut-off at $r = 5\text{Å}$ and return back to smaller distances between them in order to keep counting them as nearest neighbors. In Fig.6 we show as an example interparticle distance as a function of time for three pairs of particles, which after the period of $\sim 32ps$ move apart and distance between them increases. Note that during the time spent as nearest neighbors both particles in a pair move with opposite phases, similarly as in normal modes of dimers. In that sense those pairs of neighbors which remain the nearest neighbors for relatively long period of time in order to make an effect on high-frequency collective dynamics of the liquid can be called as quasi-bound pairs. In our simulations we identified 11 quasi-bound pairs of atoms. With increasing the cut-off or decreasing the "lifetime" of QBP their number growths rapidly. We can show that the dynamics of QBP corresponds to much faster processes, than the typical longitudinal current-current correlations. In Fig.7 we show the longitudinal current-current time correlation functions for the total mass current (tot in Fig.7) and longitudinal current autcorrelation just of the QBPs

$$F^L_{J_{QLP}J_{QLP}}(k,t) = \langle J^L_{QLP}(-k,t) J^L_{QLP}(k,0) \rangle \ . \qquad (4)$$

Here the dynamic variable of the longitudinal current of QLP is

$$J^L_{QLP}(k,t) = \frac{m}{k\sqrt{2N_{QLP}}} \sum_j^{N_{QLP}} [(\mathbf{k}\mathbf{v}^j_1)e^{-i\mathbf{k}\mathbf{r}^j_1} - (\mathbf{k}\mathbf{v}^j_2)e^{-i\mathbf{k}\mathbf{r}^j_2}] \ , \qquad (5)$$

N_{QLP} is the number of QLP identified in AIMD, index j corresponds to the j-th pair with particles 1 and 2 in it. The strong decay of the longitudinal QBP current autcorrelation after 0.3 ps is connected with the average over the whole production run, not just over the "lifetime" of the quasi-bound pairs. There is a need to derive more correct sampling of QBP with their creation/annihilation with simultaneous annihilation/creation of non-bounded particles.

Having the autocorrelation functions of QBP current (4) and (5) we can calculate the corresponding spectral function $C^L_{QBP}(k,\omega)$ and to estimate the dispersion of corresponding modes from its peak positions. In Fig.8 we compare the dispersions obtained from the longitudinal current spectral function $C^L(k,\omega)$ (for total mass current) and $C^L_{QBP}(k,\omega)$ (for only QBP current). The straight dash line with the label HD corresponds to the linear hydrodynamic dispersion law with the adiabatic speed of sound estimated [18, 26] to be 1910 m/s being close to the experimental values of [6, 27]. One can see in Fig.8 that the peak positions of $C^L_{QBP}(k,\omega)$ form quite flat dispersion law in the frequency region $16 - 18 ps^{-1}$, that practically overlaps with the flat region of the dispersion of collective excitations obtained from the total spectral function $C^L(k,\omega)$. We have take into account too that the QLP-derived modes from $C^L_{QBP}(k,\omega)$ can have additional shift down in frequency due to damping because of average over the whole trajectories (not only over the QBP

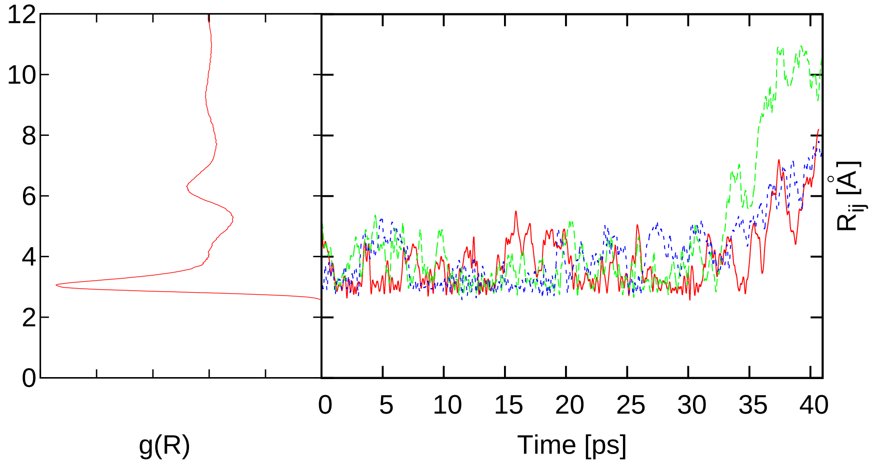

FIG. 6: Running distances between three selected pairs of Sb atoms (red solid, green dashed and blue short-dash lines in the right frame) implying quasi-bound states in time windows of ~ 30 ps. The quasi-bound states were selected among all the pairs of particles staying for not less than 30 ps within the distance $R_{ij} \leq 5$Å , which correspond to the nearest neighbors within the shoulder region of $g(R)$ in the left frame.

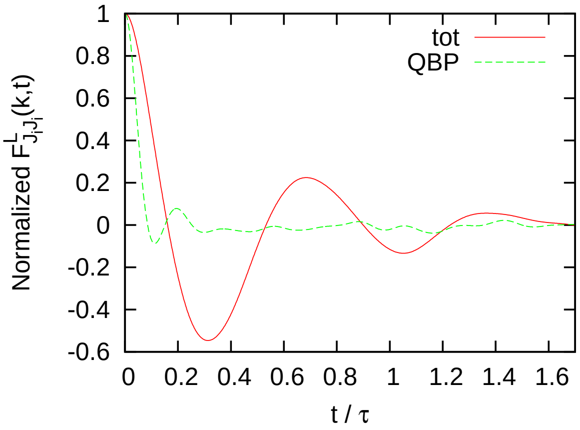

FIG. 7: Longitudinal autocorrelation functions of total current (solid line) and of current of quasi-bound atoms (dashed line) make evidence of different time scale of corresponding collective modes. The time scale τ is 1.64377 ps.

”lifetime”). Therefore it is reasonable to connect the extended flat region of the dispersion of collective excitations, observed in IXS experiments [6] and in previous AIMD simulations [7] for liquid Sb, to be caused by QLP of Sb atoms. Formation of quasi-bound pairs in a liquid leads to the emergence of the extended flat region of wave numbers close to the

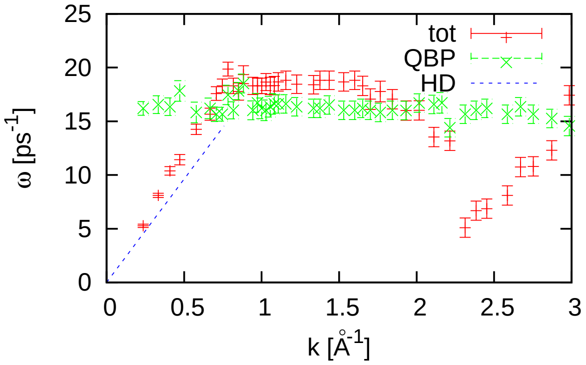

FIG. 8: Dispersions of collective modes obtained from peak positions of spectral functions of the total current (solid line) and of current of quasi-bound atoms (dashed line). The short-dash line correspond to hydrodynamic dispersion law with the adiabatic speed of sound 1910 m/s [6, 27].

boundary of the pseudo-Brillouin zone.

CONCLUSION

We performed AIMD simulations of liquid Sb with a purpose to understand the role of quasi-bound pairs of atoms in the dispersion of collective excitations. First we performed a theoretical GCM analysis of the dynamic eigenmodes in the simulated system, that resullted in two types of propagating eigenmodes. Then, we observed 11 pairs of atoms, distance in which between the neighbors remained within the region of the first coordination shell and its shoulder on pair distribution function ($R_{ij} \leq 5$Å) over at least 30 ps. We constructed from these quasi-bound pairs of Sb atoms current autocorrelation functions and corresponding spectral functions, which resulted in a flat (in the whole k-range) dispersion of propagating modes connected with the QLP. This

The existence of quasi-bound pairs poses a requirement to generalized hydrodynamics to account for their effect on density and current fluctuations. Perhaps a promising direction is an extension od the hydrodynamic treatment of chemically reacting fluids [8–10]. A related problem is how to treat at the sampling of spatial-Fourier components of particle density or current density from AIMD the breakdowsn of a quasi-bound pair when two particles begin to diffuse independently, i.e. when describing the system as a binary mixture of quasi-localized pairs and independent particles is so far unclear how to sample creation/annihilation of quasi-localized pairs in a form of dynamic variable of QLP density or QLP current. Similar problem is in the case of molecular-to-atomic fluid transition in fluid Hydrogen under pressure [28]. Our generalized hydrodynamic treatment of this kind of complex fluids will be reported elsewhere.

Acknowledgment

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