

# ***Ab initio* study of collective dynamics in the liquid phase of the equimolar alloy CsAu: Evidence for a nonmetallic state**

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The long-standing issue of a possible molten-salt-like state in the equimolar liquid alloy Cs-Au is discussed on the basis of an *ab initio* study of its collective dynamics at  $T = 913$  K and three pressures. The dispersions of the longitudinal and transverse collective excitations for all pressures were calculated by a combination of *ab initio* simulations and the method of generalized collective modes (GCMs). A fit-free GCM analysis of contributions to the concentration dynamic structure factors and the existing gap between the long-wavelength longitudinal (LO) and transverse (TO) optical branches give evidence that the liquid alloy CsAu at ambient pressure reveals typical molten-salt-like features of its collective dynamics. Increasing pressure causes the reduction of the LO-TO gap and leads to metallization of the compressed liquid CsAu.

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## **I. INTRODUCTION**

The stoichiometric crystalline compound CsAu has been known for a long time as a semiconductor with a band gap of  $\sim 2.6$  eV despite being composed of two perfect conductors.<sup>1,2</sup> Scalar-relativistic *ab initio* calculations of the electronic structure of CsAu and RbAu in the CsCl structure<sup>3</sup> resulted for CsAu in an indirect electron gap of 1.22 eV. Although some disagreement between the calculations and experiment was observed, it was attributed to the local density approximation applied in the first-principles calculations.

Liquid  $\text{Cs}_x\text{Au}_{1-x}$  alloys exhibit even more interesting electronic structure and change of conducting properties with concentration. Experimental measurements of the electric conductivity of the liquid alloys  $\text{Cs}_x\text{Au}_{1-x}$  in the whole range of molar composition<sup>4</sup> revealed a strong drop by three orders of magnitude at equimolar composition, which was supposedly connected with the emergence of a fully ionic liquid state with  $\text{Cs}^+$  and  $\text{Au}^-$  ions. A simple ionic model with  $z_{\text{Cs}} = +1$  and  $z_{\text{Au}} = -1$  was applied in Ref. 5 for satisfactory reproduction of the experimental static structure factor of equimolar liquid CsAu at temperature  $T = 913$  K measured in neutron diffraction experiments.<sup>6,7</sup> Molecular dynamics (MD) simulations for the equimolar liquid alloy CsAu therefore were based on a pairwise ionic interaction model suggested later on in Ref. 8. This model was also able to reproduce the experimental static structure factor  $S(q)$  of the equimolar CsAu liquid alloy. Another ionic model based on Tosi-Fumi potentials was suggested in Ref. 9 and applied in a detailed study of the structure of liquid CsAu by molecular dynamics simulations. The electric conductivity of liquid CsAu as a function of temperature was studied in Refs. 10 and 11 by equilibrium and nonequilibrium molecular dynamics simulations, and good agreement was obtained with the experimental data.<sup>12</sup>

The dynamic structure factors and collective excitations of  $\text{Cs}_x\text{Au}_{1-x}$  with  $x = 0.4$  and  $0.5$  were studied experimentally in Ref. 13 by means of inelastic neutron scattering. Only small differences were observed between the spectra of the two samples, despite the fact that there was a difference in conductivity of nearly two orders of magnitude. Dynamic

structure factors and collective excitations in molten  $\text{Cs}_x\text{Au}_{1-x}$  have not been studied to date by computer simulations.

However the classical simulations cannot answer the question of whether the liquid CsAu is a metallic or semimetallic (with low-density free electrons) or molten-salt-like (with localized electrons and long-range ionic interactions) system, because classical simulations *a priori* discriminate between the metallic and ionic types of system by the choice of effective interatomic potentials. Only *ab initio* simulations and analysis of quantities that are sensitive to the differences between metallic and ionic systems can solve the problem. As an example, the concentration dependence of the conductivity<sup>4</sup> recently was reproduced by *ab initio* simulations in Ref. 14.

Dynamic properties of liquids are extremely sensitive to the type of effective interaction between particles. Therefore one of the possibilities to discriminate between the metalliclike and molten-salt-like system is a simulation study of time correlation functions and collective excitations in the liquid systems of interest. It was shown in Ref. 15 that molten salts as typical Coulomb liquids have specific features of their charge-charge (or concentration-concentration) time correlation functions  $F_{cc}(k, t)$ , where  $k$  denotes the wave number. Due to the long-range Coulomb interaction the functions  $F_{cc}(k, t)$  have in the long-wavelength region ( $k \rightarrow 0$ ) a nonvanishing contribution from charge waves (optical-like modes), which is in complete contrast with the hydrodynamic behavior of the concentration autocorrelation functions in metallic alloys and Lennard-Jones mixtures.<sup>16</sup> Analytical treatment of the long-wavelength limit for  $F_{cc}(k, t)$  in Coulomb liquids within the rigid-ion model<sup>15</sup> gave evidence that the nonvanishing contribution from nonhydrodynamic charge waves in the  $k \rightarrow 0$  limit was even stronger than that from a relaxation process connected with ionic conductivity. These predictions were completely supported in classical<sup>17</sup> and *ab initio*<sup>18–20</sup> simulations of molten salts.

Another specific feature of Coulomb liquids is the gap existing in the long-wavelength limit between the longitudinal (LO) and transverse (TO) optical excitations. *Ab initio* simulations performed for NaCl,<sup>18</sup> NaI,<sup>19</sup> LiF and RbF,<sup>20</sup> and LiBr,<sup>21</sup> and parameter-free calculations of the spectra of collective excitations, gave evidence that screening by

the electron density caused a softening of the longitudinal-optical-like branch with respect to the rigid-ion case in the long-wavelength limit approximately by a factor of  $\sqrt{\epsilon_\infty}$ , where  $\epsilon_\infty$  is the high-frequency dielectric permittivity of the system. Even with the softening effects, the gap between the long-wavelength longitudinal- and transverse-optical-like excitations for all the studied molten salts was well defined. It is important to note that the LO-TO gap is a consequence of the long-range Coulomb interactions in ionic systems without conducting electrons. In regular metallic systems the ions are perfectly screened by the electron density, causing Friedel oscillations and leading to a specific oscillating decay of the effective interparticle interaction  $\sim \cos(2k_F r)/r^3$  where  $k_F$  is the Fermi momentum.<sup>22</sup> Hence there are no effective interatomic long-range Coulomb interactions that could cause the difference in frequencies of the long-wavelength LO and TO excitations in metalliclike systems.

To date precise *ab initio* calculations of the dispersions of collective excitations in liquid metals and alloys are very rare, in contrast to the numerous *ab initio* studies of phonons in crystals.<sup>23</sup> For the case of liquids one cannot obtain the dispersion of collective excitations in the same way as in crystals because the atoms do not have stable equilibrium positions in liquids. A method of instantaneous normal modes (INMs) was developed for liquids;<sup>24</sup> however one cannot calculate the dispersion of collective excitations within the INM method. For this purpose one has to calculate dynamic structure factors and analyze them by an appropriate approach based on generalized hydrodynamics.<sup>25,26</sup> Alternatively one can perform an analysis of the *ab initio* MD-derived density-density time correlation functions that are connected with dynamic structure factors via the time-Fourier transformation.<sup>22</sup> To date only the studies based on orbital-free *ab initio* MD permit well-converged time correlation functions to be obtained for systems with a large number of particles, and the precise analysis of the peak positions of the calculated dynamic structure factors and current spectral functions.<sup>27–30</sup> However this kind of *ab initio* simulations is mainly limited to the case of simple metals and their mixtures. Here for the case of *ab initio* calculation of the dynamics of molten CsAu we will apply the approach of generalized collective modes<sup>31,32</sup> (GCMs) which permits fit-free calculations of the spectra of collective excitations in liquids and of the nonhydrodynamic relaxation processes.<sup>33</sup> Previous applications of the GCM approach to *ab initio* calculations of the spectra of collective excitations in the molten salts NaCl,<sup>18</sup> NaI,<sup>19</sup> and LiF and RbF (Ref. 20) showed its great potential to analyze the dispersion and the damping of collective excitations as well as the contributions from relaxation processes and propagating modes to the dynamic structure factors, avoiding any fit.

Other quantities that reveal correlations between the electron density and ions in ionic and metallic systems are the electron-ion structure factors. It is worth noting that for binary liquid systems the electron-ion structure factors have not been reported except for the network-forming liquids GeSe<sub>4</sub>,<sup>34</sup> and SiO<sub>2</sub> and GeSe<sub>2</sub>,<sup>35</sup> in contrast to the numerous theoretical and experimental studies of electron-ion structure factors in pure liquids like Bi,<sup>36</sup> Mg,<sup>36,37</sup> Na and Al,<sup>38</sup> Ge,<sup>39</sup> Zn,<sup>40</sup> and Te.<sup>41</sup> We will calculate directly using *ab initio* simulations the electron-ion structure factors as statistical averages for

the CsAu alloy and compare them with the predictions of analytical theory.<sup>42,43</sup>

The parameter-free analysis of the collective dynamics and electron-ion structure factors in the equimolar liquid alloy CsAu will allow one to answer unambiguously the question of whether the liquid CsAu is a metallic alloy or a molten-salt-like system. The rest of the paper is organized as follows. The next section contains details of our *ab initio* MD simulations, the results of analysis of the collective dynamics are presented in Sec. III, and the conclusions of this study are collected in the last section.

## II. METHODOLOGY

We simulated the molten equimolar alloy CsAu by *ab initio* molecular dynamics (using the VASP package) on a Born-Oppenheimer surface having a collection of 150 particles in a cubic box under periodic boundary conditions. The effective electron-ion interaction was represented by Kresse-Hafner ultrasoft pseudopotentials<sup>44</sup> and the cutoff energy for the plane-wave expansions of wave functions was 180 eV. The exchange-correlation functional was taken within the generalized gradient approximation in the Perdew-Wang 1991 version. The pseudopotentials for Cs and Au corresponded to  $z_{\text{Cs}} = 7$  and  $z_{\text{Au}} = 11$  valence and semicore electrons per atom; hence we had 1350 electrons in simulations. The electronic density was constructed using a single  $\Gamma$  point in the Brillouin zone, which is well justified for the quite large system in our actual simulations.

We simulated three densities of molten CsAu at the temperature 913 K. First we estimated the equilibrium density for the ambient pressure  $\rho = 5109.96 \text{ kg/m}^3$ , which is very close to the value reported from *ab initio* simulations in Ref. 14. For this ambient pressure a sharp drop in conductivity of CsAu was observed.<sup>14</sup> The second system simulated in this study corresponded to the density  $\rho = 6052.80 \text{ kg/m}^3$ ,<sup>8</sup> and the pressure estimated from *ab initio* simulations for this system was 1.3 GPa. For the third system we first tried to apply a pressure  $\sim 2.6$  GPa; however, since the actual temperature was very close to the melting temperature we found that the density-density time correlation functions contained a slow relaxation typical for undercooled liquids, which made impossible the application of the GCM approach for analysis of the collective dynamics. Finally, the typical exponential decay of the density-density time correlation functions was obtained at the pressure 2.0 GPa which corresponded to the density  $\rho = 6343.33 \text{ kg/m}^3$ .

The time step for integration of the ionic equations of motion was 3 fs. The initial configurations were taken from classical MD simulations of CsAu with a rigid-ion model<sup>8</sup> and an equilibration over 5 ps was performed. The calculation runs in standard *NVT ab initio* molecular dynamics simulations permitted to have at least 21 700 configurations for statistical averages for each system. The large number of configurations was needed in order to obtain reliably converged static and time correlation functions as used for GCM analysis of the collective dynamics.

Forty-five  $k$  points were used for direct sampling of the relevant dynamical variables as well as the Fourier components of the electron density in the MD simulations for

calculations of static and time correlation functions  $F_{ij}(k, t)$ . Additional averages over all possible directions of the  $\mathbf{k}$  vectors with identical absolute values were performed. The smallest wave numbers reached in the *ab initio* simulations were  $k_{\min} = 0.314 \text{ \AA}^{-1}$ ,  $0.332 \text{ \AA}^{-1}$ , and  $0.337 \text{ \AA}^{-1}$  for systems corresponding to ambient, 1.3 GPa, and 2.0 GPa pressures, respectively. For each  $k$  point the shape of the MD-derived time correlation functions and the spectra of eigenvalues were analyzed via the corresponding dynamical models within the GCM method for longitudinal and transverse dynamics.<sup>16,45</sup>

The spectra of collective excitations and wave-number relaxation processes were calculated as the eigenvalues of the generalized hydrodynamic matrix  $\mathbf{T}(k)$ .<sup>31,32</sup> The matrix elements of  $\mathbf{T}(k)$  were calculated directly from the *ab initio* MD simulations. For the longitudinal dynamics a  $6 \times 6$  matrix  $\mathbf{T}(k)$  was constructed on the following six-variable set of dynamical variables:

$$\mathbf{A}^{(6)}(k, t) = \{n_A(k, t), n_B(k, t), J_A^L(k, t), J_B^L(k, t), \dot{J}_A^L(k, t), \dot{J}_B^L(k, t)\}, \quad (1)$$

where  $n_i(k, t)$  and  $J_i^L(k, t)$  are the regular Fourier components of the partial densities of particles and the longitudinal components of mass currents, and  $i = A, B$  denotes different species. It is worth noting that the partial particle densities and the density of the total mass current  $J_t^L(k, t) = J_A^L(k, t) + J_B^L(k, t)$  describe fluctuations of conserved quantities and belong to the set of hydrodynamic variables. The extended dynamical variables shown in (1) with overdots are the first time derivatives of the densities of the partial mass currents. For the transverse case the corresponding level of the extended hydrodynamic model is provided by the four-variable set

$$\mathbf{A}^{(4T)}(k, t) = \{J_A^T(k, t), J_B^T(k, t), \dot{J}_A^T(k, t), \dot{J}_B^T(k, t)\} \quad (2)$$

for calculations of another  $4 \times 4$  matrix  $\mathbf{T}(k)$  for the transverse dynamics. All the dynamic variables from  $\mathbf{A}^{(6)}(k, t)$  and  $\mathbf{A}^{(4T)}(k, t)$  were sampled in *ab initio* MD simulations, making possible direct calculations of the generalized hydrodynamic matrices and fit-free analysis of the collective excitations in liquid CsAu. For each  $k$  point we solved the eigenvalue problems for longitudinal (LD) and transverse (TD) dynamics

and obtained the  $k$  dependence of six (LD) and four (TD) eigenvalues, respectively. Purely real eigenvalues  $d_\alpha(k)$  correspond to wave-number-dependent relaxation processes, while complex-conjugated pairs of eigenvalues  $z_\alpha(k) = \sigma_\alpha(k) \pm i\omega_\alpha(k)$  reflect the propagating modes with dispersion  $\omega_\alpha(k)$  and damping  $\sigma_\alpha(k)$ .

### III. RESULTS AND DISCUSSION

#### A. Static structure factors

The large number of configurations permitted us to obtain very well-converged static and time correlation functions. In the left frame of Fig. 1 the Bhatia-Thornton static structure factors are shown. The total density (or “number-number”) static structure factor  $S_{tt}(k)$  has a very pronounced first sharp diffraction peak (FSDP) for the three pressures: at  $k \sim 1.83 \text{ \AA}^{-1}$  for ambient pressure,  $k \sim 1.94 \text{ \AA}^{-1}$  for pressure 1.3 GPa, and  $k \sim 1.97 \text{ \AA}^{-1}$  for pressure 2.0 GPa. For ambient pressure the amplitude of the FSDP is approximately 15%–20% smaller than for the higher pressures. For all three pressures we observed a prepeak in  $S_{tt}(k)$  at  $k \sim 1.13 \text{ \AA}^{-1}$  which is evidence of existing short-range order in the studied binary liquid system. The prepeak is much more pronounced for the high-pressure states. The “concentration-concentration” structure factor  $S_{cc}(k)$  (right frame in Fig. 1) has its first relatively high maximum at  $k \sim 1.25 \text{ \AA}^{-1}$ . There is a small change in the location of the main peak of  $S_{cc}(k)$  towards smaller wave numbers for the higher pressures, and a small decrease of its amplitude was observed. We recall that for typical simple molten salts like NaCl or NaI the FSDP of  $S_{tt}(k)$  has a rather small amplitude  $\sim 1.2$  while the main peak of  $S_{cc}(k)$  is very well pronounced and has amplitude  $\sim 0.75$ . Note that for equimolar systems the large- $k$  limit of  $S_{cc}(k)$  is  $\sqrt{c_A c_B} = 0.25$ . However, the most obvious feature of  $S_{cc}(k)$  that is present only in the ionic systems is its asymptote proportional to  $k^2$  in the long-wavelength region.<sup>46,47</sup> In *ab initio* simulations this was clearly observed for NaCl,<sup>18</sup> NaI,<sup>19</sup> and LiF and RbF.<sup>20</sup> In the inset of the right frame of Fig. 1 we compare the long-wavelength behavior of  $S_{cc}(k)$  for CsAu at all pressures. One can see that molten CsAu at ambient pressure shows very nice agreement with the asymptote proportional to  $k^2$  typical for molten salts, while

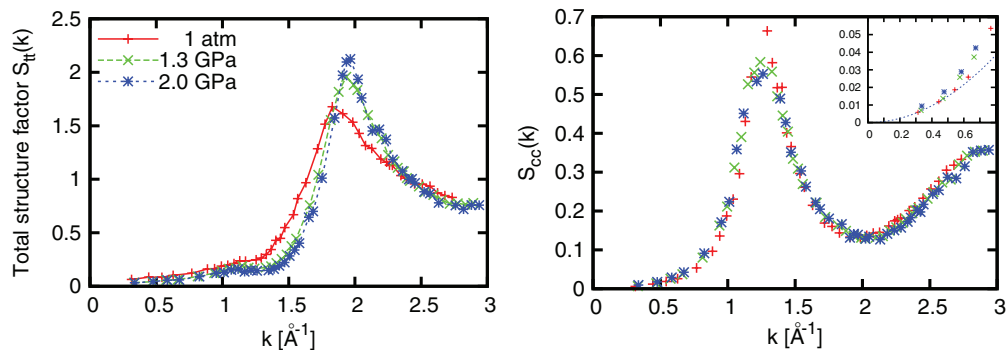


FIG. 1. (Color online) Left frame: Total static structure factors  $S_{tt}(k)$  for CsAu at 913 K at ambient pressure (plus symbols), 1.3 GPa (cross symbols), and 2.0 GPa (star symbols). Right frame: Bhatia-Thornton concentration-concentration static structure factor  $S_{cc}(k)$ . Notations are the same as in the left frame. The inset shows the long-wavelength behavior of  $S_{cc}(k)$ . The  $k^2$  asymptote specific for molten salts is shown by the dotted line.

for higher pressures one observes a deviation from such a tendency.

### B. Spectra of collective excitations

The spectra of collective excitations were calculated from the MD-derived time correlation functions using the fit-free GCM approach as was done in the previous *ab initio* studies of dynamic properties of molten salts.<sup>18–21</sup>

The dispersions of the two longitudinal and two transverse branches of collective excitations in molten CsAu for three pressures are shown in Fig. 2. The lowest transverse branch

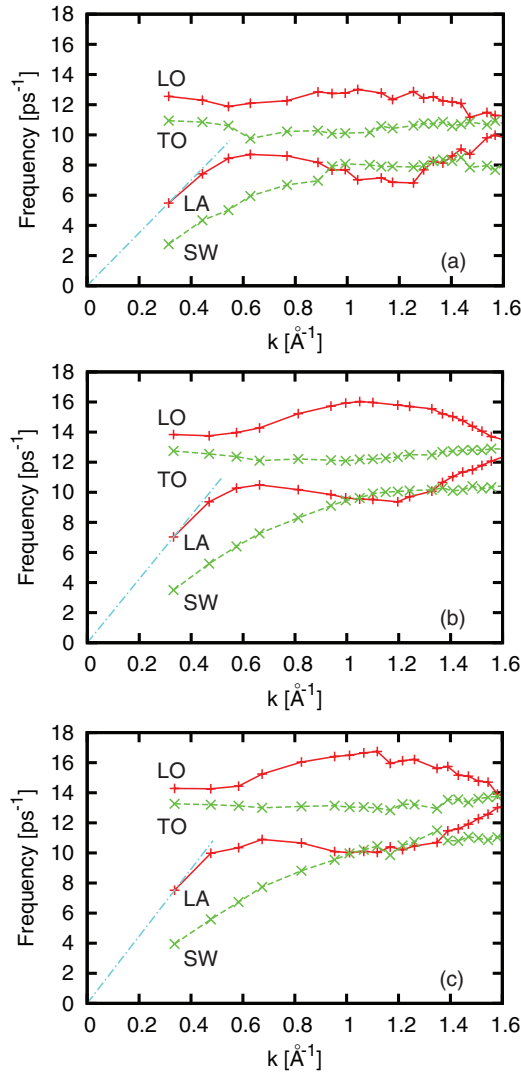


FIG. 2. (Color online) Dispersion of longitudinal and transverse collective excitations in molten CsAu at  $T = 913$  K and ambient pressure (a),  $P = 1.3$  GPa (b), and  $P = 2.0$  GPa (c), as obtained from fit-free GCM calculations based on the six-variable (1) and four-variable (2) dynamical models for longitudinal and transverse dynamics, respectively. The labels SW, LA, LO, and TO correspond to the branches of shear waves, longitudinal acoustic, and longitudinal and transverse optical excitations, respectively. For molten salts there exists a gap for the long-wavelength LO and TO excitations. The straight dashed lines correspond to a linear dispersion law with the high-frequency speed of sound given in Table I.

TABLE I. Estimations from *ab initio* simulations of the speed of sound ( $c$ ) and the frequencies of the long-wavelength longitudinal (LO) and transverse (TO) optical excitations in molten CsAu at  $T = 913$  K and three pressures

| $P$     | $c$<br>(m/s) | LO<br>(ps <sup>-1</sup> ) | TO<br>(ps <sup>-1</sup> ) | LO-TO gap<br>(ps <sup>-1</sup> ) |
|---------|--------------|---------------------------|---------------------------|----------------------------------|
| 1 atm   | 1752         | 12.55                     | 10.94                     | 1.61                             |
| 1.3 GPa | 2117         | 13.84                     | 12.74                     | 1.10                             |
| 2.0 GPa | 2231         | 14.29                     | 13.27                     | 1.02                             |

(cross symbols) corresponds to shear waves in the liquid and in the long-wavelength limit it goes to zero frequency at some nonzero wave number, because the macroscopic transverse sound modes are not supported by liquids. The longitudinal acoustic branch (shown by plus symbols) at the smallest wave number permits us to make an estimate for the high-frequency speed of sound: it increases with the pressure as shown in Table I. For wave numbers  $k > 0.5$  Å<sup>-1</sup> a coupling with another branch of longitudinal high-frequency optic excitations is observed for all pressures. This coupling shifts the acoustic branch to lower frequencies following the linear dispersion law (“negative” dispersion). The issue of possible positive and negative dispersion of acoustic modes in liquids due to coupling with structural relaxation was treated analytically in Ref. 48. However, in this case the main contribution to the negative dispersion comes from the coupling between acoustic and optical excitations, which was studied analytically in Ref. 49.

Most important for our purpose of estimation of the metallic or molten-salt-like type properties in liquid CsAu is the issue of the gap between the longitudinal and transverse optical excitations in the long-wavelength limit. Our fit-free calculations reveal that the tendency to dispersion of LO and TO branches for  $k \rightarrow 0$  gives evidence of the existence of such a LO-TO gap at ambient pressure [Fig. 2(a)] and its reduction with increasing pressure. The shift up in frequencies of the long-wavelength LO and TO modes and the reduction of the LO-TO gap with increasing pressure can be seen from Table I. Typical values for molten salts are as follows. The LO-TO gap was  $\sim 8.5$  ps<sup>-1</sup> for NaI, which has the largest calculated value of the high-frequency dielectric permittivity (electronic screening properties of an ionic charge),  $\epsilon_\infty \sim 3.59$ ,<sup>19</sup> in NaCl the gap was  $\sim 13$  ps<sup>-1</sup> with  $\epsilon_\infty \sim 2.22$ ,<sup>18</sup>, and in LiF the gap was  $\sim 24$  ps<sup>-1</sup> with the quite small  $\epsilon_\infty \sim 1.95$ .<sup>20</sup>

For the case of CsAu at ambient pressure the LO-TO gap was obtained as  $\sim 1.6$  ps<sup>-1</sup> (Table I). This small value of the LO-TO gap correlates with the rather large estimate of  $\epsilon_\infty = 8.82$  from the long-wavelength asymptotes of  $S_{cc}(k)$  obtained from *ab initio* simulations of molten CsAu and classical simulations with the rigid-ion model,<sup>8</sup> as was done before for molten salts.<sup>18–20</sup>

### C. Contributions of optical modes to the concentration dynamic structure factors

Further evidence of molten-salt-like type of dynamics for liquid CsAu at ambient pressure is the behavior of the mode contributions (called the mode strengths in Ref. 43) to the

concentration density autocorrelation functions  $F_{cc}(k, t)$  or the concentration dynamic structure factors  $S_{cc}(k, \omega)$ . Because of the electroneutrality condition in ionic systems, the relaxation process connected with concentration fluctuations does not show the typical hydrodynamic asymptote for its inverse relaxation time  $\tau_{cc}^{-1}(k) \sim k^2$ , but tends to a constant. As a result  $F_{cc}(k, t)$  in molten salts do not have in the long-wavelength region the regular simple single-exponential decay that occurs for metallic liquid alloys and non-Coulombic liquid mixtures, but contain oscillations due to the contribution from optical modes, which does not vanish in the  $k \rightarrow 0$  limit. This was shown by analytical theory and computer simulations in Ref. 15.

We obtained the wave-number-dependent mode contributions from the eigenvectors of the relevant eigenmodes of the generalized hydrodynamic matrix  $\mathbf{T}(k)$ . According to Ref. 50 the concentration dynamic structure factors constructed using the dynamic variables of (in our case)  $\mathbf{A}^{(6)}(k, t)$  is represented via mode contributions in the following way:

$$\begin{aligned} \frac{S_{cc}^{(6)}(k, \omega)}{S_{cc}(k)} &= A_{cc}^{conc}(k) \frac{2d_{conc}(k)}{\omega^2 + d_{conc}^2(k)} + A_{cc}^{str}(k) \frac{2d_{str}(k)}{\omega^2 + d_{str}^2(k)} \\ &+ \sum_{\alpha=1}^2 \left[ B_{cc}^{\alpha}(k) \frac{\sigma_{\alpha}(k)}{[\omega - \omega_{\alpha}(k)]^2 + \sigma_{\alpha}^2(k)} \right. \\ &\left. + D_{cc}^{\alpha}(k) \frac{\omega - \omega_{\alpha}(k)}{[\omega - \omega_{\alpha}(k)]^2 + \sigma_{\alpha}^2(k)} \right] \end{aligned} \quad (3)$$

with the real  $k$ -dependent amplitudes of mode contributions from relaxation processes connected with mutual diffusivity  $A_{cc}^{conc}(k)$  and structural relaxation  $A_{cc}^{str}(k)$ , and symmetric  $B_{cc}^{\alpha}(k)$  and asymmetric  $D_{cc}^{\alpha}(k)$  contributions from the  $\alpha$ th collective excitation. In (3)  $d_{conc}(k)$  and  $d_{str}(k)$  correspond to real eigenvalues describing diffusive and structural relaxations, while  $\omega_{\alpha}(k)$  and  $\sigma_{\alpha}(k)$  are the frequencies and damping of the acoustic and optical modes.

For the case of molten-salt-like dynamics the mode strengths behave in the long-wavelength region as follows:

$$A_{cc}^{conc}(k \rightarrow 0) \rightarrow 1 - \Delta, \quad B_{cc}^{opt}(k \rightarrow 0) \rightarrow \Delta, \quad (4)$$

where the nonzero constant  $\Delta$  is expressed via the “bare” frequency of the optical mode and the inverse lifetimes of the optical and relaxing modes.<sup>15</sup> The optical modes have a contribution to  $S_{cc}(k, \omega)$  that does not vanish in the long-wavelength limit for molten salts. For ordinary liquid mixtures there is no contribution from the optical-like modes to  $S_{cc}(k, \omega)$  in the hydrodynamic limit and  $\Delta \equiv 0$ . In Fig. 3 the amplitudes of the symmetric contributions from optical excitations,  $B_{cc}^{opt}(k)$ , are compared for molten CsAu at three different pressures. From the mode strengths of the optical modes one can estimate that for ambient pressure  $B_{cc}^{opt}(k)$  tends in the long-wavelength limit to  $\Delta \sim 0.12$ , which is typical for the molten-salt-like state. For molten CsAu at higher pressures the mode strengths  $B_{cc}^{opt}(k \rightarrow 0)$  show a decrease towards zero, which indicates a tendency to metallization with increasing pressure. We stress that these results for wave-number-dependent mode contributions to the concentration dynamic structure factors were calculated directly from eigenvectors associated with

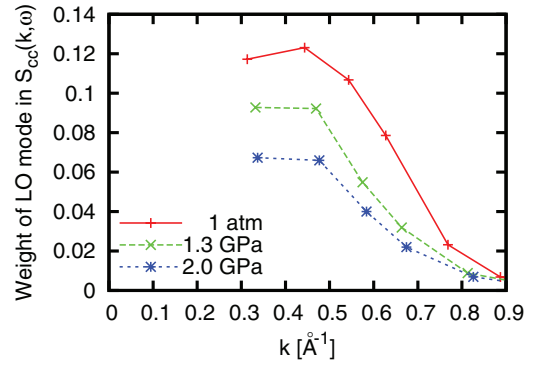


FIG. 3. (Color online) Wave-number-dependent contributions (3) to the concentration dynamic structure factor  $S_{cc}(k, \omega)$  from LO modes,  $B_{cc}^{opt}(k)$ , for liquid CsAu at  $T = 913$  K and three pressures. Typical for the molten salts is a contribution from LO modes to  $S_{cc}(k, \omega)$  that does not vanish in the limit  $k \rightarrow 0$  (Refs. 15 and 19).

the relevant dynamic eigenmode, i.e., no fit was used in this analysis.

#### D. Electronic properties

The electronic densities of states calculated for liquid CsAu at three pressures from our *ab initio* simulations are shown in Fig. 4. We applied a smearing of the eigenvalues with Gaussians having the parameter  $\sigma_{el} = 0.05$  eV, as is standard for the *ab initio* simulations of molten salts. For ambient pressure the calculated electronic density of states (DOS) is very similar to the results<sup>14</sup> obtained for a system of only 54 atoms. The narrow band located  $\sim 10$  eV below the Fermi level corresponds to the  $5p$  electrons of Cs. This band changes its location with respect to the Fermi level only slightly with increasing pressure. The high density of states in the energy range  $\sim 3$ – $4$  eV below the Fermi level comes from the  $5d$  electrons of Au, while closer to the Fermi level the  $5d$  states are strongly hybridized with  $6s$  electrons. The  $5d$  band shifts to lower energies with respect to  $E_F$  with increasing pressure. Of most interest is the issue of a possible gap at the Fermi level. For all pressures we observed a pseudogap at the Fermi level, although the empty  $6s$  band of Cs is right above the Fermi level and it can easily be filled by electrons because of temperature effects leading to semimetallic behavior of the conductivity.

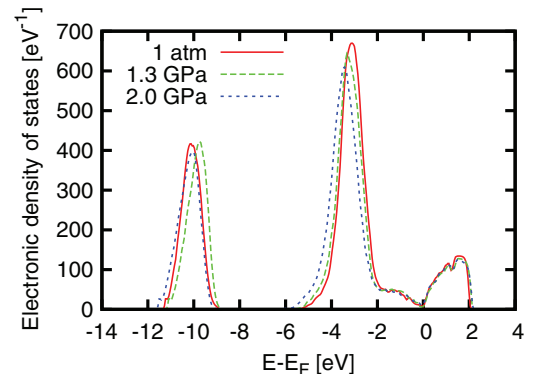


FIG. 4. (Color online) Density of electronic states for liquid CsAu at 913 K and three pressures.

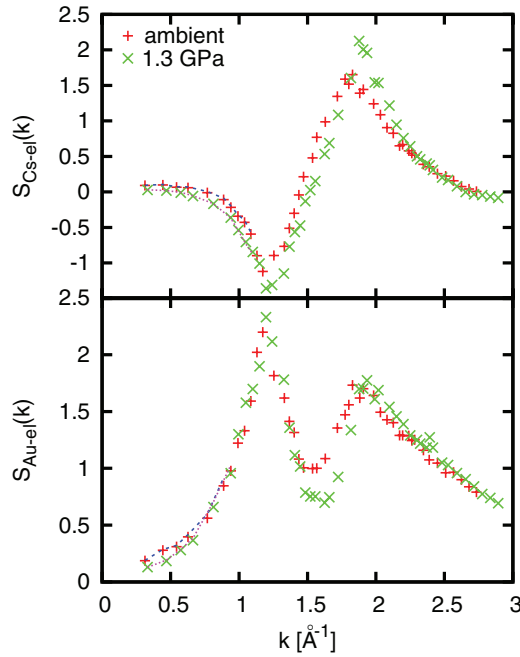


FIG. 5. (Color online) Partial electron-ion structure factors  $S_{Cs-el}(k)$  and  $S_{Au-el}(k)$  calculated directly from *ab initio* molecular dynamics for ambient pressure and  $P = 1.3$  GPa. The lines represent the analytical expressions (5) for the long-wavelength behavior of partial electron-ion structure factors in binary alloys (Ref. 42).

In Fig. 5 we show with symbols the partial electron-ion structure factors  $S_{i-el}(k) = \langle n_i(k)n_{el}(-k) \rangle$  calculated directly via statistical averages from the Fourier components of the partial ion and electron densities obtained in *ab initio* simulations. The partial electron-ion structure factors show opposite tendencies for Cs and Au in the region of wave numbers corresponding to the location of the maximum of  $S_{cc}(k)$ . In order to check the reliability of the calculated electron-ion structure factors we compared  $S_{i-el}(k)$  with analytical expressions for the long-wavelength limit of the electron-ion structure factors.<sup>42,43</sup>

$$\begin{aligned} \lim_{k \rightarrow 0} S_{Cs-el}(k) &= \frac{1}{\sqrt{z_{tot}}} [z_{Cs} \sqrt{N_{Cs}} S_{CsCs}(k) + z_{Au} \sqrt{N_{Au}} S_{CsAu}(k)], \\ \lim_{k \rightarrow 0} S_{Au-el}(k) &= \frac{1}{\sqrt{z_{tot}}} [z_{Cs} \sqrt{N_{Cs}} S_{CsAu}(k) + z_{Au} \sqrt{N_{Au}} S_{AuAu}(k)], \end{aligned} \quad (5)$$

where  $z_i$  is the number of valence electrons corresponding to a pseudopotential of type  $i = \text{Cs, Au}$ , and  $z_{tot} = N_{Cs}z_{Cs} + N_{Au}z_{Au}$  is the total number of electrons in our simulations. It is seen from Fig. 5 that the analytical expressions (5) reproduced the calculated partial electron-ion structure factors in a quite wide region of wave numbers—up to  $k \sim 1 \text{ \AA}^{-1}$ .

For typical molten salts the long-wavelength asymptotes of the partial ionic structure factors  $S_{ij}(k)$  should be identical and as follows from expressions (5) the same should be true for electron-ion structure factors. In this sense the stronger shift of  $S_{Cs-el}(k)$  at ambient pressures to positive values on approaching

the long-wavelength region results in the 2.3 times smaller ratio of  $S_{Au-el}(k)$  and  $S_{Cs-el}(k)$  for the smallest  $k$  point than the value at pressure 1.3 GPa. This is further evidence of the close similarities of the structural properties of the electron distribution in molten CsAu at ambient pressure with the case of molten salts.

#### IV. CONCLUSIONS

We studied the collective dynamics of the equimolar liquid alloy CsAu by *ab initio* simulations and the GCM methodology of calculation of dynamic eigenmodes in liquid systems and their contributions to the concentration dynamical structure factors. We aimed to look at specific collective dynamical quantities that are very sensitive to the existence of the interatomic long-range interactions in liquids. This approach showed its ability to estimate for the equimolar liquid alloy CsAu a molten-salt-like state at ambient pressure and reduction of the characteristic quantities of such a state with pressure. The main results of this study are as follows:

(i) At ambient pressure we observed for liquid CsAu nice agreement with the asymptotic behavior (proportional to  $k^2$ ) of the concentration-concentration static structure factor, which is a specific feature of ionic systems. Increasing pressure caused a deviation from this asymptotic behavior of  $S_{cc}(k)$ .

(ii) A gap between longitudinal and transverse optical long-wavelength excitations of  $\sim 1.6 \text{ ps}^{-1}$  was obtained at ambient pressure from the calculated dynamical eigenmodes. The existing LO-TO gap for optical modes is a feature observed before in simple molten salts by the GCM approach.<sup>18–21</sup> For higher pressures we noted a tendency to reduction of the gap between LO and TO frequencies in the long-wavelength limit.

(iii) The predictions of the analytical theory<sup>15</sup> on the non-vanishing contribution from long-wavelength optical modes to the concentration dynamic structure factors of molten salts were checked in the case of liquid CsAu. We observed in the long-wavelength region the obviously nonvanishing contribution  $B_{cc}^{opt}(k \rightarrow 0) \equiv \Delta \sim 0.12$  from the optical-like excitations to  $S_{cc}(k, \omega)$  for CsAu at ambient pressure, which supports the indications of a molten-salt-like state in CsAu.

(iv) We calculated in *ab initio* simulations the electron-ion structure factors and observed perfect agreement in the region  $k < 1 \text{ \AA}^{-1}$  between the calculated  $S_{i-el}(k)$  and analytical long-wavelength expressions for binary liquids.<sup>42</sup>

Our results (i)–(iv) are consistent and unambiguously show that the equimolar liquid CsAu at ambient pressure is a molten-salt-like system. Increasing pressure reduces all the specific molten-salt-like features in the dynamics, giving evidence of possible metallization of the binary liquid alloy CsAu at high pressures.

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