

Pressure-induced emergence of unusually high-frequency transverse excitations in a liquid alkali metal: Evidence of two types of collective excitations contributing to the transverse dynamics at high pressures

Taras Bryk, G. Ruocco, T. Scopigno, and Ari P. Seitsonen

Citation: *The Journal of Chemical Physics* **143**, 104502 (2015); doi: 10.1063/1.4928976

View online: <http://dx.doi.org/10.1063/1.4928976>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/143/10?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[Pressure-induced polymerization of P\(CN\)₃](#)

J. Chem. Phys. **142**, 194503 (2015); 10.1063/1.4919640

[Entropy-scaling laws for diffusion coefficients in liquid metals under high pressures](#)

J. Appl. Phys. **117**, 135903 (2015); 10.1063/1.4916986

[First-principles study of liquid gallium at ambient and high pressure](#)

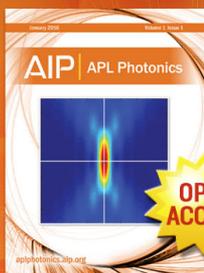
J. Chem. Phys. **135**, 044507 (2011); 10.1063/1.3615936

[Collective dynamics in a liquid polyvalent metal: Liquid thallium at the melting point](#)

J. Chem. Phys. **132**, 074504 (2010); 10.1063/1.3319500

[Pressure-induced structural and chemical changes of solid HBr](#)

J. Chem. Phys. **111**, 1595 (1999); 10.1063/1.479420



Launching in 2016!

The future of applied photonics research is here

**OPEN
ACCESS**

AIP | APL
Photonics

Pressure-induced emergence of unusually high-frequency transverse excitations in a liquid alkali metal: Evidence of two types of collective excitations contributing to the transverse dynamics at high pressures

Taras Bryk,^{1,2} G. Ruocco,^{3,4} T. Scopigno,^{3,5} and Ari P. Seitsonen^{6,7}

¹*Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Street, UA-79011 Lviv, Ukraine*

²*Lviv Polytechnic National University, 12 S. Bandera Street, UA-79013 Lviv, Ukraine*

³*Dipartimento di Fisica, Universita di Roma La Sapienza, 5 Piazzale Aldo Moro, I-00185 Roma, Italy*

⁴*Center for Life Nano Science @Sapienza, Istituto Italiano di Tecnologia, 295 Viale Regina Elena, I-00161 Roma, Italy*

⁵*IPCF-CNR, c/o Universita di Roma La Sapienza, 5 Piazzale Aldo Moro, I-00185 Roma, Italy*

⁶*Département de Chimie, Université de Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

⁷*Département de Chimie, École Normale Supérieure, 24 rue Lhomond, F-75005 Paris, France*

(Received 19 June 2015; accepted 10 August 2015; published online 8 September 2015)

Unlike phonons in crystals, the collective excitations in liquids cannot be treated as propagation of harmonic displacements of atoms around stable local energy minima. The viscoelasticity of liquids, reflected in transition from the adiabatic to elastic high-frequency speed of sound and in absence of the long-wavelength transverse excitations, results in dispersions of longitudinal (L) and transverse (T) collective excitations essentially different from the typical phonon ones. Practically, nothing is known about the effect of high pressure on the dispersion of collective excitations in liquids, which causes strong changes in liquid structure. Here dispersions of L and T collective excitations in liquid Li in the range of pressures up to 186 GPa were studied by *ab initio* simulations. Two methodologies for dispersion calculations were used: direct estimation from the peak positions of the L/T current spectral functions and simulation-based calculations of wavenumber-dependent collective eigenmodes. It is found that at ambient pressure, the longitudinal and transverse dynamics are well separated, while at high pressures, the transverse current spectral functions, density of vibrational states, and dispersions of collective excitations yield evidence of two types of propagating modes that contribute strongly to transverse dynamics. Emergence of the unusually high-frequency transverse modes gives evidence of the breakdown of a regular viscoelastic theory of transverse dynamics, which is based on coupling of a single transverse propagating mode with shear relaxation. The explanation of the observed high-frequency shift above the viscoelastic value is given by the presence of another branch of collective excitations. With the pressure increasing, coupling between the two types of collective excitations is rationalized within a proposed extended viscoelastic model of transverse dynamics. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4928976>]

INTRODUCTION

The collective dynamics in liquid metals and alloys, despite being one of the fascinating problems of condensed matter physics,^{1,2} is not yet completely understood on microscopic spatial and time scales. The longitudinal collective excitations in liquids are well defined at small wave numbers k and frequency ω where due to small damping (which according to hydrodynamic theory increases with wave number as $\sim k^2$), they make visible (peak or a shoulder at non-zero frequency) contribution to the dynamic structure factors $S(k, \omega)$ and corresponding longitudinal current spectral function,

$$C^L(k, \omega) = \frac{\omega^2}{k^2} S(k, \omega). \quad (1)$$

Relation (1) is a consequence of the continuity equation. Transverse collective excitations are not sustained by liquids on macroscopic length scales (or small wave numbers);

however, transverse non-hydrodynamic collective excitations called shear waves emerge at some non-zero wave number k_s ,^{3,4} and can manifest at larger wave numbers as a peak on the shape of the transverse current spectral function $C^T(k, \omega)$.

Upon the success of the hydrodynamic theory in explanation of the three-peak shape of the scattered intensity of light in liquids,^{5,6} several generalized schemes were proposed to describe the dynamic structure factors of pure liquids on the boundary and outside the hydrodynamic regime obtained from the inelastic neutron scattering (INS) and X-ray scattering (IXS) experiments as well as by molecular dynamics (MD) simulations.⁷⁻⁹ Local and non-local mode coupling approaches¹⁰⁻¹³ were applied to explanation of a deviation of the dispersion of the longitudinal collective modes with increasing wave numbers from the hydrodynamic linear dispersion $\omega_{hyd}(k) = c_s k$, where c_s is the adiabatic speed of sound. Intensive theoretical studies based on extended kinetic theory¹⁴⁻¹⁶ and viscoelastic memory function approach¹⁷⁻¹⁹ revealed features of the short-wavelength longitudinal collec-

tive excitations, which can even exist outside the first pseudo-Brillouin zone in liquids and were also obtained from the analysis of the inelastic neutron scattering experiments.^{20,21}

Only recently have experimental,^{22–26} theoretical,^{27–29} and simulation studies^{30–33} started to focus on revealing the non-hydrodynamic modes in collective dynamics of liquids that can be observed in the shape of dynamic structure factors only outside the hydrodynamic region. The hydrodynamic regime of collective dynamics of liquids means relaxation and propagating processes that are constrained by local conservation laws valid on sufficiently large spatial and time scales.^{34,35} In the hydrodynamic regime, the liquid behaves as continuum without revealing its atomistic structure, while outside the hydrodynamic region, on spatial scales comparable with mean interatomic distance, the effects of non-hydrodynamic structural relaxation as well as non-hydrodynamic propagating modes like shear and heat waves become very important for the collective dynamics.³⁶

Recently, there have appeared reports on possible manifestation of non-hydrodynamic shear waves on dynamic structure factors $S(k, \omega)$ of liquid Ga, measured in inelastic scattering experiments,^{23,37} and longitudinal current spectral function $C^L(k, \omega)$ of liquid Sn, calculated from *ab initio* molecular dynamics (AIMD) simulations.³⁸ Later on, an analysis of the IXS experiments on liquid Sn³⁹ gave evidence that a superposition of two damped harmonic oscillator (DHO) spectral shapes describes the experimental spectra better than a single DHO fit, and additional analysis of the experimental current spectral functions $C^L(k, \omega)$, performed with a two-Gaussian fit, showed good agreement with the *ab initio* simulation results. Note that in Refs. 23 and 37, the observed signal from the supposed shear waves to the shape of experimental $S(k, \omega)$ was deduced from a simple comparison of dispersions of longitudinal (L) and transverse (T) collective excitations obtained in AIMD simulations. No theoretical analysis of the possibility for transverse excitations in the shape of the dynamic structure factor was performed in Refs. 23 and 37. Although the possible emergence of a signal from shear waves in the light scattering spectrum in molecular liquids was discussed in the 1970s,^{35,40–43} there have appeared no simulation studies to support this phenomena. Only in water, the coupling between longitudinal and transverse collective excitations and their manifestations in both L and T current spectral functions were studied by MD simulations⁴⁴ which were supported in recent experimental study.⁴⁵ Hence, the case of L-T coupling in single-component liquid metals is very exotic and so far, there are neither models for the analysis nor explanations of its origin.

In simple liquid alkali metals, there have been no indications at all of possible L-T coupling, like it was suggested in polyvalent metals.^{23,37,38} Although recent *ab initio* simulation studies of liquid metals under high pressures^{46–48} revealed numerous features in structural, electronic, and single-particle dynamic properties, the dynamic structure and dispersion of collective excitations in liquid metals under high pressure remain completely unexplored. Especially interesting is the case of liquid Li, where for a liquid alkali metal, an exotic tetrahedral clustering at pressures above 150 GPa was observed.⁴⁷ So far, no studies have been performed to clarify how the

pressure-induced changes in structure affect the collective dynamics in liquid metals. Only recently there appeared a report on a dynamical crossover in liquid Rb at pressures ~ 13 GPa,⁴⁹ however, a detailed analysis of the spectra of collective excitations was not performed. For the case of solids, the studies of the phonon spectra at high pressures are of great interest, especially for iron at the earth's core pressures.⁵⁰

Another motivation for this combined simulation and theoretical study is in the absence of theoretical schemes which would satisfactorily describe contributions from two types of collective excitations in spectral functions either measured in experiments or calculated from simulations. The suggested from IXS experiment contributions of the transverse excitations to the dynamic structure factors^{23,37} are not based on some theory, and it is not clear which cross-correlations would be responsible for this new effect, because for simple liquids, the longitudinal and transverse currents are statistically independent with zero cross-correlators. Therefore, even application of simplest dynamical models to analysis of collective dynamics of liquid systems, where the L-T coupling can be visible, is of great interest because they can point out the direction of future theoretical studies in order to disclose the mechanism responsible for emergence of the L-T coupling at some conditions in pure liquids. Even account for the higher number of exact sum rules will be interesting to apply in this study of collective dynamics in liquid metal under high pressure.

Hence, the aim of this study is to evaluate pressure-induced features in the longitudinal and transverse collective excitation spectra of liquid Li, which is a simple liquid metal at ambient pressure and undergoes at the pressure ~ 150 GPa a structural transition to a liquid with tetrahedral short-range order^{47,51} with very non-uniform distribution of electron density.⁵³ Such a strong change in structure of the liquid Li with pressure should be reflected in the dynamic properties of the systems and in particular in the behavior of collective excitations. We will rationalize the spectra of collective excitations using the direct estimation of the L/T dispersion from the corresponding current spectral functions calculated in AIMD as well as from the models of generalized hydrodynamics. The remaining paper is organized as follows. In the next section we give the details of the *ab initio* simulations and direct estimation of the dispersion of L and T collective excitations in the studied pressure range. Theoretical analysis of the AIMD-derived time correlation functions are reported in “Theoretical Analysis of Collective Dynamics”: we will apply the thermo-viscoelastic (VE) model for analysis of the longitudinal dynamics, as well as the standard and extended viscoelastic (EVE) models for the transverse case. The Conclusions of this study are given in the last section.

AB INITIO SIMULATIONS

We have performed *ab initio* molecular dynamics simulations for liquid Li at temperature 1000 K and seven pressures ranging from 1 atm to 186 GPa. The highest studied pressure was chosen to be higher than the pressure of the reported, in Ref. 47, tetrahedral clustering in liquid Li. For comparison, at the high pressure of ~ 180 GPa and temperature 1000 K, *ab initio* simulations of fluid hydrogen⁵² gave evidence of

rapidly increasing DC electronic conductivity that implied metallization of hydrogen fluid. In simulations, we used systems of 300 particles (at pressures up to 68 GPa) and 600 particles (at higher pressures) in the NVT ensemble. Production runs over 12 000 time steps (the time step in simulations was 1 fs) were performed for each pressure after equilibrations over 3–4 ps. The electron-ion interactions were represented by the all-electron projector augmented-wave (PAW) potentials.^{54,55} For all pressures, the generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) version⁵⁶ was applied in order to account for exchange-correlation effects in the strongly non-uniform (all-electron) density of molten Li. The cut-off energy for the expansion of wave functions in plane waves was 271.65 eV. The electron density was constructed using the single Γ point in the Brillouin zone that is justified by quite large box size.

For calculations of the k -dependent static and time correlation functions up to sixty wave numbers k were sampled with all possible directions of the corresponding wave vectors. The smallest wave numbers in our simulations ranged from $k_{min} = 0.353 \text{ \AA}^{-1}$ for liquid Li at ambient pressure to $k_{min} = 0.442 \text{ \AA}^{-1}$ at pressure of 186 GPa. The calculated k -dependent static and time correlation functions were averaged over all possible directions of wave vectors with the same absolute value.

The calculated density-density and L/T current-current time correlation functions as well as their Fourier transforms contain all the information about the collective dynamics in the studied systems. The side peak at non-zero frequency ω of the dynamic structure factor $S(k, \omega)$ or the peaks of the longitudinal and transverse current spectral functions $C^{L,T}(k, \omega)$ are usually used for a simple numerical estimate of the dispersion law of L and T collective excitations. In Fig. 1, we show the qualitative change of the current spectral functions $C^{L,T}(k, \omega)$ at low and high pressures: 1 atm and 186 GPa.

The longitudinal current spectral functions $C^L(k, \omega)$ tend to zero in the zero-frequency limit according to (1), while the transverse current spectral functions $C^T(k, \omega)$ at zero frequency start from finite values, defined by the wavenumber-dependent shear viscosity $\eta(k)$ via

$$C^T(k, 0) = \frac{k_B T}{m} \frac{\rho}{k^2 \eta(k)},$$

where k_B , ρ , and m denote Boltzmann constant, mass density, and atomic mass, respectively. In the long-wavelength limit, the generalized shear viscosity $\eta(k)$ tends to the macroscopic value of η for the studied liquid. The longitudinal current spectral functions $C^L(k, \omega)$ in the range of wave numbers $k < 3 \text{ \AA}^{-1}$ at all pressures show well-pronounced single peak, which for larger wavenumbers gets very smeared out. Only at the very high pressure (186 GPa) and wave numbers $k > 3 \text{ \AA}^{-1}$, $C^L(k, \omega)$ contains a shoulder at frequency $\sim 200 \text{ ps}^{-1}$. The transverse current spectral functions $C^T(k, \omega)$ in the long-wavelength region do not contain any peak because long-wavelength transverse excitations cannot be sustained by liquids. Fig. 1 gives evidence of the present shear waves in liquid Li at the ambient pressure with increasing frequency: $\sim 30 \text{ ps}^{-1}$ at $k = 1.06 \text{ \AA}^{-1}$ and $\sim 55 \text{ ps}^{-1}$ at $k = 2.39 \text{ \AA}^{-1}$,

while at higher wave numbers, the peaks of $C^T(k, \omega)$ were not observed. Increasing pressure caused interesting changes in the peak location of $C^T(k, \omega)$: in Fig. 1, one can see that at the pressure of 186 GPa, there exist low-frequency peaks (even lower in frequency than for the comparable wave numbers at ambient pressure), while at wave numbers 1.53 and 2.42 \AA^{-1} , there is clearly visible shoulder in the high-frequency region, which transforms into well-defined high-frequency peak for higher wave numbers. Interestingly, the longitudinal current spectral functions $C^L(k, \omega)$ at the highest studied pressure show weak high-frequency shoulders right in the region of frequencies where a well-pronounced high-frequency peak of $C^T(k, \omega)$ is observed. This can be an indication of the emergence of L-T coupling in liquid Li with pressure.

The dispersion of collective excitations obtained from the peak positions of the longitudinal and transverse current spectral functions $C^{L,T}(k, \omega)$ in liquid Li at pressures 1 atm, 68, 125, and 186 GPa are shown in Fig. 2. At ambient pressure, there is nothing unusual in the behaviour of L and T dispersions. At wave numbers $k > 2.4 \text{ \AA}^{-1}$, the shape of $C^T(k, \omega)$ slowly changes to a structure with a weak shoulder and higher wave number; the $C^T(k, \omega)$ is of almost Gaussian shape as it is shown in Fig. 1. This behaviour did not allow us to estimate the dispersion of T excitations for $k > 2.4 \text{ \AA}^{-1}$, that however does not mean the absence of the transverse excitations. Their contribution to $C^T(k, \omega)$ is simply much smaller than the one of relaxation processes, centered at zero frequency. The increasing pressure should cause the shift of the peak positions of $C^{L,T}(k, \omega)$ towards higher values. This is the case of longitudinal dispersion curve. In transverse excitations, we instead observe at $P = 68 \text{ GPa}$ and wave numbers $k < 2.0 \text{ \AA}^{-1}$ only low-frequency peaks of $C^{L,T}(k, \omega)$, which rapidly increased at higher wave numbers. This implies a crossover between two different low- and high-frequency dispersion curves. At pressure 125 GPa, we clearly observed at high wave numbers two branches of collective excitations contributing to $C^T(k, \omega)$, which become very pronounced at $P = 186 \text{ GPa}$. In the right frames of Fig. 2, we show the Fourier-transformed velocity autocorrelation function (VACF) $\tilde{Z}(\omega)$, which is a sum of low-frequency relaxation contributions due to diffusion and of vibrational density of states (VDOS). One can see that the main peak of VDOS shifts towards higher frequencies, while at $P = 186 \text{ GPa}$, the VDOS contains a pronounced low-frequency peak, which corresponds to the low-frequency branch of transverse excitations.

THEORETICAL ANALYSIS OF COLLECTIVE DYNAMICS

Up to this point, we have performed a standard direct estimation of the dispersion of collective excitations from the apparent peak positions of $C^{L,T}(k, \omega)$. Such a methodology is, however, not very accurate because it ignores the other contributions than the ones from propagating modes: the peak position is exactly ascribed to the frequency of the propagating L/T excitation. However, even in the case of observation of the side peaks or corresponding shoulders on the shape of dynamic structure factors $S(k, \omega)$, it is obvious that one has

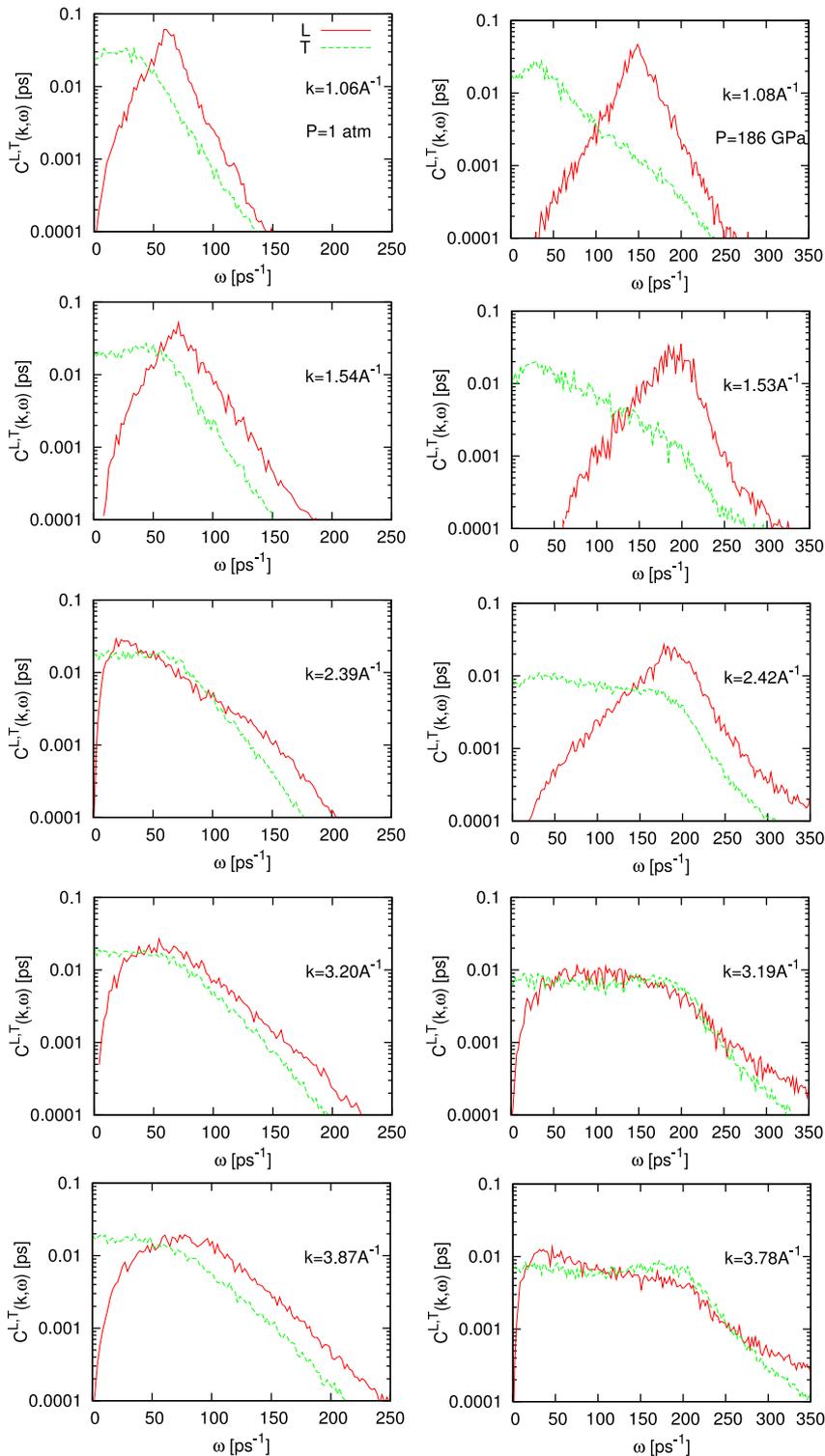


FIG. 1. Longitudinal (L) and transverse (T) current spectral functions of liquid Li at pressures 1 atm (left frames) and 186 GPa (right frames) at five wave numbers. The current spectral functions were normalized by the square of thermal velocity $k_B T/m$.

to separate first contributions from the central peak (relaxing modes) and side peaks that in simplest approximation can be done by making use of DHO-type fit² to ascribe the correct position of the side peak to the frequency of collective excitation. Namely, the main task of the generalized collective modes (GCM) methodology is in estimation of separate contributions from different relaxing and propagating modes based on eigenmode analysis. Especially important a proper theoretical analysis is in the case of transverse dynamics, because in contrast to the longitudinal case for transverse current, there

does not apply the continuity equation which automatically forces the condition $C^L(k, \omega = 0) \equiv 0$. Advanced generalized hydrodynamic methodologies can make use of the exact sum rules on frequency moments of dynamic structure factor $S(k, \omega)$: there exist standard approaches which satisfy the sum rules up to the fourth frequency moment in pure¹⁰ and binary⁵⁷ liquids, as well as more sophisticated ones valid up to the eighth frequency moment of $S(k, \omega)$.^{58,59} Another possibility is to improve the low-frequency behaviour of the model $S(k, \omega)$ in order to get better agreement with the

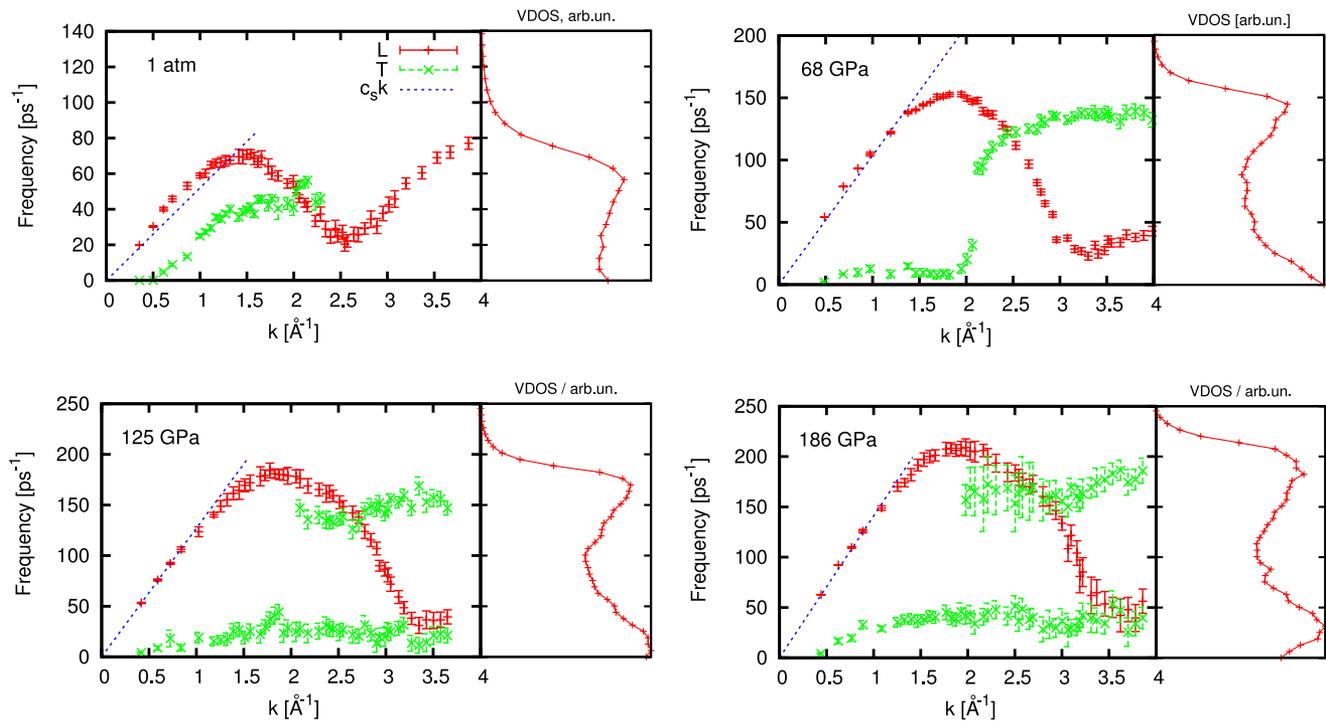


FIG. 2. Dispersion of longitudinal (L) and transverse (T) collective excitations in liquid Li at pressures 1 atm, 68, 125, and 186 GPa. The dashed line corresponds to hydrodynamic dispersion law with adiabatic speed of sound. The right frames show the Fourier-transformed VACFs, which contain beyond the low frequencies the vibrational density of states.

MD-derived one as suggested in Ref. 60 by making use of the time moments of the density-density time correlation function. A methodology of calculation of the spectra of collective excitations in liquids, known as the GCM, is based on calculation of relaxing and propagating eigenmodes of the system using a matrix form of the generalized Langevin equation, which is the master equation for time correlation functions. This methodology was proposed in Refs. 61 and 62 and developed for practical applications in connection with classical and *ab initio* simulations.^{63,64} It permits to recover from the eigenvectors associated with relaxing and propagating eigenmodes the shape of the simulation-derived time correlation functions, hence yielding information about the dispersion of collective excitations and contributions of different relaxing and propagating processes to the spectral functions of interest. Another advantage of the GCM approach is in many analytical results obtained for relaxing and propagating modes outside the hydrodynamic region,³⁶ which allow the interpretation of general MD data on dynamic properties.

Thermo-viscoelastic model for longitudinal dynamics

The longitudinal dynamics in simple liquids outside the hydrodynamic regime can be well described by a thermo-viscoelastic five-variable dynamic model,

$$\mathbf{A}^{(5)}(k, t) = \{n(k, t), J^L(k, t), e(k, t), J^T(k, t), \dot{e}(k, t)\}, \quad (2)$$

where $n(k, t)$, $J^L(k, t)$, and $e(k, t)$ are the Fourier-components of hydrodynamic variables of particle density, density of longitudinal component of mass current, and energy density, respectively. The overdots in the extended dynamic variables

in (2) correspond to the first time derivatives of hydrodynamic variables. Since the static equilibrium average of cross-correlations between a dynamic variable and its first time derivative is equal to zero—they are statistically independent and the extension of the hydrodynamic basis set with the time derivatives of hydrodynamic variables can be useful in describing non-hydrodynamic processes. Thermo-viscoelastic model (2) is practically equivalent to the memory-function approach within the account for the second-order memory function for density fluctuations and the first-order memory function for energy fluctuations, although additional sum rules for the zeroth time-moments of corresponding density-density, density-energy, and energy-energy time correlation make the GCM approach more precise from the point of view of the number of exact sum rules satisfied.⁶²

In general, within the GCM approach,⁶² the chosen extended set of N dynamic variables is used for construction of an $N \times N$ generalized hydrodynamic matrix $\mathbf{T}(k)$, eigenvalues $z_j(k)$ of which correspond to wave-number dependent collective modes. Analytical solutions of the thermo-viscoelastic dynamic model in long-wavelength limit were reported in Ref. 28. The generalized hydrodynamic matrix $\mathbf{T}(k)$ is expressed in the following way:⁶²

$$\mathbf{T}(k) = \mathbf{F}(k, t=0) \tilde{\mathbf{F}}^{-1}(k, z=0) \quad (3)$$

via the $N \times N$ matrices of static correlation functions $\mathbf{F}(k, t=0)$ and of Laplace-transformed time correlation functions in Markovian approximation $\tilde{\mathbf{F}}(k, z=0)$.

For the case of the five-variable set of dynamic variables of thermo-viscoelastic model (2), one has to calculate directly from AIMD for each sampled wave number k the 5×5

matrices,

$$\mathbf{F}(k, t = 0) = \begin{pmatrix} f_{nn} & 0 & f_{ne} & -ikf_{JJ} & 0 \\ 0 & f_{JJ} & 0 & 0 & -if_{Je} \\ f_{ne} & 0 & f_{ee} & -if_{Je} & 0 \\ ikf_{JJ} & 0 & if_{Je} & f_{JJ} & 0 \\ 0 & if_{Je} & 0 & 0 & f_{\dot{e}\dot{e}} \end{pmatrix} \quad (4)$$

and

$$\tilde{\mathbf{F}}(k, z = 0) = \begin{pmatrix} \tau_{nn}f_{nn} & \frac{i}{k}f_{nn} & \tau_{ne}f_{ne} & 0 & f_{ne} \\ \frac{i}{k}f_{nn} & 0 & \frac{i}{k}f_{ne} & f_{JJ} & 0 \\ \tau_{nn}f_{ne} & \frac{i}{k}f_{ne} & \tau_{ee}f_{ee} & 0 & f_{ee} \\ 0 & -f_{JJ} & 0 & 0 & if_{Je} \\ -f_{ne} & 0 & -f_{ee} & if_{Je} & 0 \end{pmatrix}, \quad (5)$$

where the indices in matrix elements correspond to dynamic variables from set (2). For simplicity, we show explicitly imaginary matrix elements in (4) and (5). Almost all matrix elements are the static correlation functions, which should be estimated from AIMD, and only three quantities in the matrix $\tilde{\mathbf{F}}(k, z = 0)$ keep information on time-dependent processes in the system—these are the so-called wave-number-dependent correlation times,

$$\tau_{ij}(k) = \frac{1}{F_{ij}(k, t = 0)} \int_0^\infty F_{ij}(k, t) dt, \quad i, j = n, e.$$

Hence, having the trajectories, velocities, and forces on particles during the AIMD run, we can easily calculate the static correlators between $n(k, t)$, $J^L(k, t)$, and $J^T(k, t)$ as well as the correlation time $\tau_{nn}(k)$. The other matrix elements $f_{ne}(k)$, $f_{ee}(k)$, $f_{Je}(k)$, and $f_{\dot{e}\dot{e}}$ and two correlation times $\tau_{ne}(k)$ and $\tau_{ee}(k)$ can be calculated directly from AIMD only when dynamic variables $e(k, t)$ and $\dot{e}(k, t)$ were directly sampled in simulations, that is, extremely time consuming in contrast to classical MD simulations with effective pair potentials.⁵⁹ Therefore, these six quantities can be treated as fitting parameters. The fitting procedure used in this study was described in detail in Ref. 63. The pairs of complex-conjugated eigenvalues $z_j^\pm(k) = \sigma_j(k) \pm i\omega_j(k)$ of the generalized hydrodynamic matrix $\mathbf{T}(k)$ correspond to the collective excitations (propagating eigenmodes) with dispersion $\omega_j(k)$ and damping $\sigma_j(k)$.

In Fig. 3, we show the dispersion of the acoustic longitudinal collective excitations in liquid Li at pressure 125 GPa. The propagating eigenmodes of the thermo-viscoelastic model (star symbols) perfectly agree with the observed peaks of the longitudinal current spectral function $C^L(k, \omega)$ up to the wave numbers $\sim 2.6 \text{ \AA}^{-1}$. For higher wave numbers, the fitting procedure based on the thermo-viscoelastic dynamic model $\mathbf{A}^{(5)}$ became unstable with large deviations for eigenvalues with increasing k -values. One of the reasons of the observed failure of the fitting procedure at large wave numbers can be the effect of the transverse collective excitations, which for the pressure 125 GPa is observed on the shape of $C^T(k, \omega)$ as two branches for wave numbers higher than $\sim 2.1 \text{ \AA}^{-1}$ —see Fig. 2. In case of the emerging with pressure coupling between short-wavelength L and T collective modes, the thermo-viscoelastic

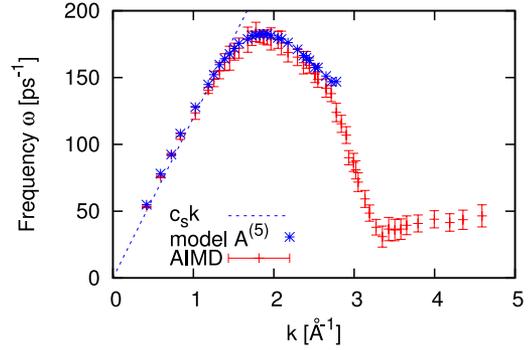


FIG. 3. Dispersion of collective excitations in liquid Li at pressure 125 GPa as follows from the analysis of $C^L(k, \omega)$ (plus symbols with error bars) and from the complex eigenmodes of the thermo-viscoelastic model $\mathbf{A}^{(5)}$ (star symbols). The dashed line corresponds to hydrodynamic dispersion law with adiabatic speed of sound.

dynamic model $\mathbf{A}^{(5)}$, which does not take into account coupling to transverse dynamics, is unable to correctly describe the complex collective dynamics in the highly pressurized liquid Li. In fact, in case of the liquid Li at the ambient pressure (see Fig. 2), the regular decoupled behavior of the L and T branches was observed, and the GCM results for liquid Li at ambient pressure reported in Ref. 63 showed the ability of the thermo-viscoelastic dynamic model $\mathbf{A}^{(5)}$ to describe the longitudinal collective excitations in the short-wavelength region. By date, there is no theoretical description of the possible coupled L-T dynamics in liquids, only a few simulation observations were reported in the literature^{23,38} for liquid polyvalent metals. Below, we will suggest an extended viscoelastic model for the transverse dynamics, which will be able to describe the existence of the two branches of collective excitations contributing to the shape of the corresponding time correlation functions.

Another important feature of the application of the thermo-viscoelastic dynamic model $\mathbf{A}^{(5)}$ in connection with *ab initio* simulation is a possibility to estimate the adiabatic speed of sound and hydrodynamic dispersion law (straight dashed line in the long-wavelength region in Fig. 3) using the extrapolation of the k -dependent ratio of

$$c_s = \sqrt{\frac{k_B T}{m}} \lim_{k \rightarrow 0} \sqrt{\frac{\gamma(k)}{S(k)}},$$

where the wave-number-dependent ratio of specific heats $\gamma(k) = C_p(k)/C_v(k)$ is expressed via the matrix elements $f_{ij}(k)$ in the following way:^{61,62}

$$\gamma(k) = 1 + \frac{1}{k^2} \frac{[f_{Je}(k)f_{nn}(k) - kf_{ne}(k)]^2}{f_{ee}(k)f_{nn}(k) - f_{ne}^2(k)},$$

and $f_{nn}(k) = S(k)$ is the structure factor. This methodology of the *ab initio* calculation of the macroscopic adiabatic speed of sound was proposed in Ref. 63 and used for the case of liquid Li at ambient pressure and liquid Rb in a wide range of pressures.⁴⁹ Note that the existing methodology of the *ab initio* estimation of the adiabatic speed of sound for fluids via the numerical calculation of the Landau-Placzek ratio⁶⁷ is quite sophisticated and requires smooth dynamic structure factors $S(k, \omega)$ and a methodology how to separate contributions to

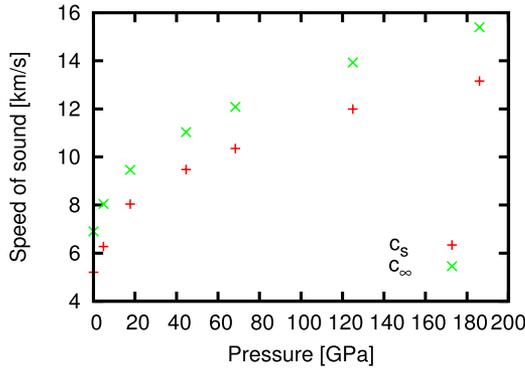


FIG. 4. Pressure dependence of the adiabatic c_s and high-frequency (elastic) c_∞ speeds of sound for the liquid Li.

the central and side peaks. In Fig. 4, the pressure dependence of the adiabatic speed of sound c_s is shown together with the values of the high-frequency speed of sound c_∞ calculated directly from the AIMD data in the standard way from the relation,

$$\lim_{k \rightarrow 0} \frac{\langle j^L(-k)j^L(k) \rangle}{\langle J^L(-k)J^L(k) \rangle} \propto c_\infty^2 k^2.$$

The existence of two characteristic for liquids macroscopic values of the speed of sound is the important feature of the viscoelasticity of liquids. In particular, a viscoelastic effect known as the positive sound dispersion depends on the ratio c_∞/c_s .²⁸ The ratio of the high-frequency speed to the adiabatic speed of sound in liquid Li is a little higher than unity, slightly decreases with pressure from ~ 1.2 at the ambient pressure to ~ 1.16 at $P = 186$ GPa, that according to Ref. 28 gives evidence of a small positive dispersion in liquid Li in a wide pressure range.

Viscoelastic model for transverse dynamics

In order to rationalize the pressure-induced changes in the transverse dynamics, being more pronounced than the ones in longitudinal case, we first make a check of the regular viscoelastic behaviour in the ambient pressure state. The viscoelastic behaviour in transverse dynamics means purely exponential shear relaxation on macroscopic distances, i.e., absence of the macroscopic transverse acoustic modes, while on nanoscales, the shear wave propagation can take place. Hydrodynamic model is unable to describe shear waves, because on macroscopic scale, there exists only a single transverse conserved quantity—transverse component of momentum density and corresponding single balance equation for it. In order to obtain propagating solutions for transverse dynamics, one has to consider at least a system of two coupled balance equations.⁶⁵

The standard VE model for transverse dynamics in liquids^{3,4,65} is based on the simplest extension of the hydrodynamic approach by improving the short-time behaviour of the transverse current autocorrelation functions $F_{JJ}^T(k, t)$ up to the precision of the second frequency moment of $C^T(k, \omega)$. This is done by considering a system of two equations: in addition to the hydrodynamic equation for the conserved transverse

component of mass-current $J^T(k, t)$, one considers another balance equation for its first time derivative,

$$j^T(k, t) \equiv ik\sigma^T(k, t),$$

where $\sigma^T(k, t)$ are the transverse components of the stress tensor. The transverse components were taken from microscopic expressions for the mass-current and its first time derivative,

$$\mathbf{J}(k, t) = \frac{m}{\sqrt{N}} \sum_{i=1}^N \mathbf{v}_i(t) e^{-i\mathbf{k}\mathbf{r}_i(t)},$$

$$\dot{\mathbf{J}}(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N [\mathbf{F}_i(t) + im(\mathbf{k}\mathbf{v}_i)\mathbf{v}_i(t)] e^{-i\mathbf{k}\mathbf{r}_i(t)},$$

where m is the atomic mass of Li, $\mathbf{r}_i(t)$, $\mathbf{v}_i(t)$, and $\mathbf{F}_i(t)$ are the position, velocity, and force acting on the i th particle along the AIMD trajectories. Hence, the first time derivative of the transverse current being a dynamic variable statistically independent with $J^T(k, t)$ because of the general properties of dynamic variables $A(k, t)$ in classical statistical mechanics³⁴

$$\langle A(-k, t) \frac{\partial}{\partial t} A(k, t) \rangle = \langle A(-k, t) \dot{A}(k, t) \rangle \equiv 0 \quad (6)$$

permits treatment of dynamic processes which are completely absent in the hydrodynamic viscous regime. Moreover, since $J^T(k, t)$ contains microscopic forces acting on the particle, it enables description of the elastic properties of the fluids and correct treatment of viscoelastic transition. The generalized hydrodynamic matrix $\mathbf{T}(k)$ of the two-variable viscoelastic model of transverse dynamics is very simple,

$$\mathbf{T}^{(2T)}(k) = \begin{pmatrix} 0 & -1 \\ \omega_{bare}^2(k) & \omega_{bare}^2(k)\tau_{JJ}^T(k) \end{pmatrix}. \quad (7)$$

Here, the square of “bare” (as for a non-damped process) transverse frequency is³⁰

$$\omega_{bare}^2(k) = k^2 G(k) / \rho \equiv \frac{\langle j^T(-k)j^T(k) \rangle}{\langle J^T(-k)J^T(k) \rangle},$$

with $G(k)$ being the wave number-dependent high-frequency shear modulus. The correlation time $\tau_{JJ}^T(k)$ is estimated at each k -point from AIMD-derived time correlation functions, and at the long-wavelength limit, its asymptotic behaviour is $\tau_{JJ}^T(k \rightarrow 0) \sim k^{-2}$. Calculation of the dynamic eigenmodes of generalized hydrodynamic matrix the system of two equations results in two relaxing modes in the long-wavelength region (viscous regime) or a pair of damped shear waves (elastic regime).^{3,4} The wave number k_s , at which propagating eigenmodes emerge in the system, defines the propagation gap for shear waves in liquid, because for $k < k_s$, shear waves are not sustained by the liquid,^{3,68}

$$k_s = \frac{\sqrt{\rho G}}{2\eta}.$$

Here G , η , and ρ are the macroscopic high-frequency shear modulus, shear viscosity, and mass density, respectively. Hence, the viscoelastic theory of transverse dynamics yields viscous behaviour without any transverse (sound) propagating modes on macroscopic length scales and emergence of shear waves at nonzero wave number k_s . The dispersion of the shear

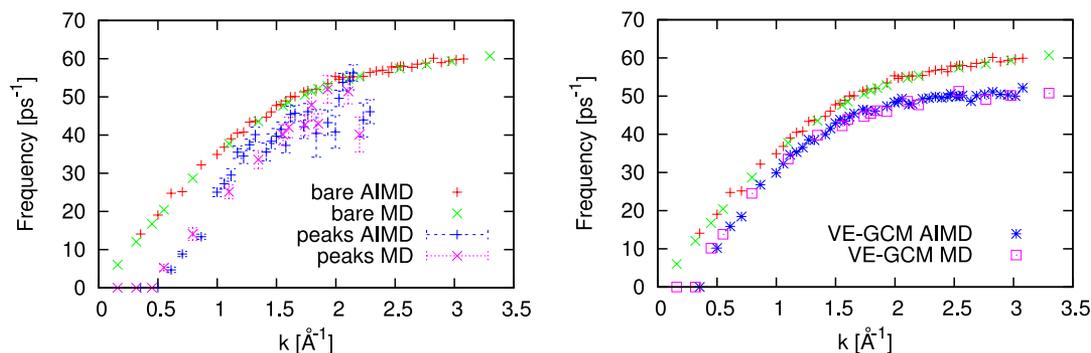


FIG. 5. “Bare” frequencies, peak positions of $C^T(k, \omega)$, and viscoelastic (VE) GCM eigenvalues for transverse dynamics in liquid Li at 1000 K and at ambient pressure. The transverse current spectral functions $C^T(k, \omega)$ do not show any peak at non-zero frequency at $k > 2.39 \text{ \AA}^{-1}$.

waves is defined by the elastic high-frequency shear modulus and in general form is expressed as a renormalization of a “bare” frequency due to dissipation processes which cause damping of oscillations,

$$\omega^T(k) = [\omega_{bare}^2(k) - \sigma^2(k)]^{1/2}. \quad (8)$$

Here, $\sigma(k)$ is the damping of shear waves due to coupling of “bare” transverse propagating modes with shear relaxation. Hence, the dispersion of shear waves is always lower in frequency than the dispersion of “bare” modes. In Fig. 5, we show the dispersion of “bare” modes, peak positions of $C^T(k, \omega)$, and GCM eigenvalues in VE model, calculated from the AIMD and classical MD simulations with effective pair potentials performed with 3300 particles. One can see that the both kinds of simulations are in perfect agreement for “bare” frequencies, peak positions, and GCM eigenvalues. The VE theory works perfectly in liquid Li at ambient pressure: the peak positions of $C^T(k, \omega)$ and GCM eigenvalues have lower frequencies than the elastic “bare” dispersion, and there exists a propagation gap for shear waves in the long-wavelength region because the long-wavelength transverse sound excitations are not supported in liquids.

Qualitatively different results are obtained from the comparison of the “bare” dispersion, VE eigenvalues, and peak positions of $C^T(k, \omega)$ at high pressures. The behaviour of the VE eigenvalues at pressure 125 GPa (cf. Fig. 6) is in disagreement at $k > 0.8 \text{ \AA}^{-1}$ with the observed peak positions of $C^T(k, \omega)$. Moreover, the second, or high-frequency branch of collective excitations, that is observed at $k > 2 \text{ \AA}^{-1}$ as high-frequency peaks of $C^T(k, \omega)$, is located at frequencies that are higher than the “bare” elastic dispersion. This is possible only if another branch of collective excitations exists, which due to coupling to the transverse one shifts it toward higher frequencies. Hence, the breakdown of the regular VE description of transverse dynamics at high frequencies is a consequence of two branches of collective excitations contributing to transverse dynamics.

Extended viscoelastic model for transverse dynamics

In order to rationalize the AIMD findings and the inability of the viscoelastic model to describe the observed peak positions of $C^T(k, \omega)$ at high pressures, we have applied more sophisticated extended dynamic models with more

coupled dynamic variables for transverse dynamics. Within the standard memory-function approach,⁶⁵ one can systematically improve a theoretical expression for a time correlation function by taking into account higher-order memory functions that is equivalent to better reproduction of the short-time behaviour of the time correlation function constraining it to the corresponding higher number of exact sum rules. Within the GCM approach, which is essentially based on the same memory-function formalism in matrix form, the higher-order sum rules will be fulfilled by extension of the set of dynamic variables by their time derivatives.⁶² In the analysis of transverse dynamics of liquid Li at high pressure, it appeared that the further extension of the VE model with “fast” dynamic variables generated via the higher (second and third) time derivatives of the transverse current, like it was done in Refs. 59 and 68, leads to further improvement of short-time behaviour of the transverse current-current time correlation functions; however, this improvement of the short-time behaviour does not allow to recover the correct oscillations of $F_{JJ}^T(k, t)$ at high pressures. Another possibility for generalized hydrodynamic treatment is to improve the low-frequency behaviour of the theoretical description of dynamic structure factors or current spectral functions by adding into the GCM scheme some “slow” dynamic variables.⁶⁰ This generalisation was successfully applied in the study of low-frequency dynamics in a binary metallic glass.⁶⁶

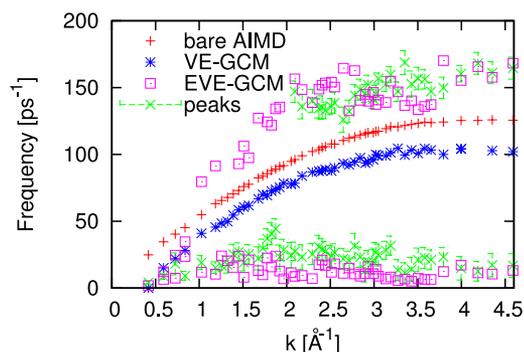


FIG. 6. Frequencies of transverse collective excitations in liquid Li at $P = 125 \text{ GPa}$ and $T = 1000 \text{ K}$: directly obtained from AIMD “bare” frequencies and peak positions of $C^T(k, \omega)$, and GCM eigenvalues obtained within the regular viscoelastic (VE) theory and extended viscoelastic (EVE) theory with two types of collective excitations.

In order to represent the non-hydrodynamic “slow” variables (for transverse dynamics, the only conserved quantity is the transverse component of total momentum), we can represent them by making use of integral relations in the following hierarchy:

$$\begin{aligned} I^1 J^T(k, t) &\equiv I J^T(k, t) = \int_{C_1}^t J^T(k, t') dt', \\ I^2 J^T(k, t) &= \int_{C_2}^t I J^T(k, t') dt', \\ &\vdots \\ I^s J^T(k, t) &= \int_{C_s}^t I^{s-1} J^T(k, t') dt', \end{aligned} \quad (9)$$

where C_s are arbitrary constants.⁶⁰ This way of construction of “slow” dynamic variables corresponds to the general relations between slower and faster statistically independent dynamic variables in GCM approach as

$$A_{\text{fast}}(k, t) = \frac{\partial}{\partial t} A_{\text{slow}}(k, t)$$

that permits to extend the hierarchy of collective processes like in Eq. (6) in the case when the “fast” dynamic variable $A_{\text{fast}}(k, t)$ is the hydrodynamic one of particle density or transverse mass-current density. It is obvious that the “slow” dynamic variables one cannot sample directly in MD simulations because of integral relations (9). However, all the static averages and relevant time moments⁶⁰ can be calculated from the MD-derived time correlation functions simply as

$$\begin{aligned} \langle I J^{T*}(k) J^T(k) \rangle &= \int_0^\infty F_{JJ}^T(k, t) dt \equiv \tau_{JJ}^T(k), \\ \langle I^2 J^{T*}(k) J^T(k) \rangle &= -\langle I J^{T*}(k) I J^T(k) \rangle \\ &= \int_0^\infty t F_{JJ}^T(k, t) dt \equiv \tau_{JJ}^{2T}(k). \end{aligned} \quad (10)$$

The way of construction of slow dynamic variables (9) permits to obtain for the time correlation function identically the same expression as in the regular GCM approach as the sum of separable N_v mode contributions.⁶⁶ In the case of the N_v -variable dynamic model for glass systems, the GCM replica has the following expression

$$F_{ij}^{(N_v)}(k, t) = \sum_{\alpha=1}^{N_v} G_{ij}^{\alpha}(k) e^{-z_{\alpha}(k)t}. \quad (11)$$

In our case of the transverse dynamics in high-pressure liquid Li one can extend the initial transverse viscoelastic model (two-variable dynamic model) by several “slow” dynamic variables (9). It appears that one can introduce a transverse analogy for the regular density-density time correlation functions, which can be a time correlation function constructed on simplest slow extended transverse dynamic variables

$$F_{II}^T(k, t) = \langle I J^{T*}(k, 0) I J^T(k, t) \rangle. \quad (12)$$

It is obvious that this time correlation function is connected via the second time derivative to the standard transverse current autocorrelation function:

$$-\frac{\partial^2}{\partial t^2} F_{II}^T(k, t) \equiv F_{JJ}^T(k, t),$$

and the time Fourier-transform of $F_{II}^T(k, t)$ is right the transverse analogy of dynamic structure factor $S^T(k, \omega)$ suggested in Ref. 69.

We applied the EVE scheme with five ($N_v = 5$) dynamic variables,

$$A^{(5T)}(k, t) = \{I^3 J^T(k, t), I^2 J^T(k, t), I J^T(k, t), J^T(k, t), j^T(k, t)\} \quad (13)$$

for calculations of the dynamic eigenmodes contributing to the shape of $F_{JJ}^T(k, t)$ via (11). Note that a basis set of at least four dynamic variables is needed in order to obtain two pairs of complex eigenvalues corresponding to propagating eigenmodes with the purpose of checking our suggestion that the effect of unusually high-frequency transverse excitations comes from the coupling with another branch of collective excitations. Set (13) containing five dynamic variables allows for another purely real eigenvalue contributing at low frequencies in $C^T(k, \omega)$. In general, the proposed theoretical scheme EVE of analysis of AIMD-derived time correlation functions allows to recover three (0th, 1st, and 2nd) frequency moments of $C^T(k, \omega)$ (as in the regular VE approach) and additionally seven (from the 0th to the 6th) time moments

$$\langle t^n \rangle(k) = \frac{1}{n!} \int_0^\infty t^n F_{JJ}^T(k, t) dt$$

of the AIMD-derived time correlation function $F_{JJ}^T(k, t)$.^{60,66} The generalized hydrodynamic matrix $\mathbf{T}^{(5T)}(k)$ generated for transverse five-variable dynamic model (13) was used in the analysis of dynamic eigenvalues and eigenvectors contributing to corresponding time correlation functions (11).

In Fig. 7, we show how accurately this EVE scheme permits to recover the AIMD-derived transverse time correlation functions in the example case of liquid Li at $P = 125$ GPa. In contrast to the regular VE description, which results in only one type of transverse collective excitations with wrong dispersion law (star symbols in Fig. 6) and corresponding wrong minimum location of the transverse current autocorrelation function $F_{JJ}^T(k, t)$ (long-dashed line in the right frame of Fig. 7), the extended GCM scheme (EVE) with five dynamic variables perfectly recovers the AIMD-derived $F_{JJ}^T(k, t)$ and results in two types of propagating modes with frequencies (open squares in Fig. 6) which

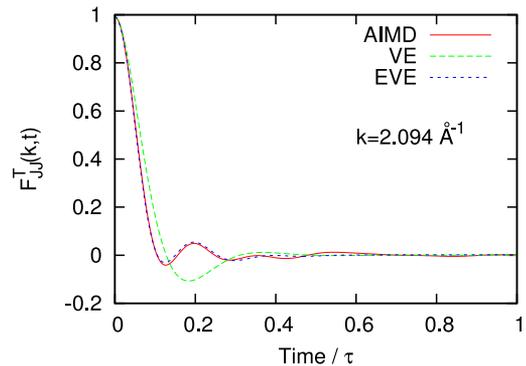


FIG. 7. Transverse current autocorrelation functions obtained from AIMD (solid line), the VE (long-dashed line) and EVE (short-dashed line) models of generalized hydrodynamics for liquid Li at $P = 125$ GPa and $T = 1000$ K. The time scale τ is equal to 0.218 126 ps.

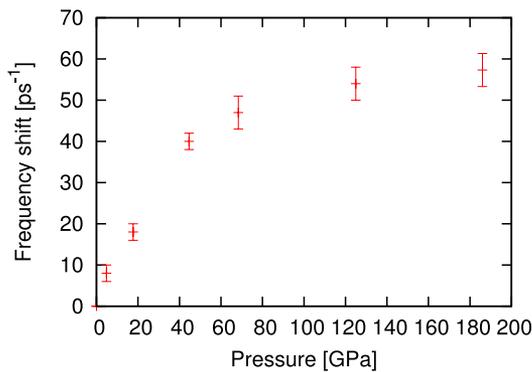


FIG. 8. The pressure dependence of a shift from viscoelastic (VE) frequency (8) to the observed high-frequency peak position of the $C^T(k, \omega)$ that can be treated as an intensity of coupling between the two types of collective modes.

correspond well to the peak positions of the $C^T(k, \omega)$. Hence, the theoretical scheme based on the extended viscoelastic theory is able to recover the AIMD-derived transverse current autocorrelation functions by means of contributions from two types of collective excitations.

In general, one can treat the up shift of the frequency of transverse excitations from its viscoelastic value as a consequence of coupling with another low-frequency branch of collective excitations. In Fig. 8, the pressure dependence of this shift shows a rapid increase with pressure that gives evidence of the pressure-induced intensity of coupling between the two types of collective modes.

CONCLUSIONS

In summary, we have obtained by *ab initio* simulations and generalized hydrodynamic models, the dispersion of longitudinal and transverse collective excitations in liquid Li at $T = 1000$ K in the pressure range up to 186 GPa. Our results enable one to observe the pressure-induced, strongly non-spherical change in the dispersions and macroscopic values of the adiabatic and elastic speeds of sound. We have observed the emergence of the two contributions (low- and high-frequency ones) from collective excitations to transverse current spectral function $C^T(k, \omega)$ in liquid Li with increasing pressure. These AIMD findings are supported by the pronounced two-peak structure of the vibrational density of states at pressure 186 GPa.

We have shown that only in the low-pressure liquid, the regular viscoelastic model of transverse dynamics is able to yield correctly GCM eigenvalues in agreement with the peak positions of $C^T(k, \omega)$, while at high pressures, only the extended viscoelastic model with two types of coupled collective excitations explains the unusually high-frequency transverse current correlations in liquid Li. The observed weak shoulders of $C^L(k, \omega)$ at high pressures nearly at the frequencies corresponding to the location of the high-frequency transverse branch implied the mutual effect also for the L-branch of collective excitations, i.e., the possible pressure-induced emergence of the L-T coupling in liquid Li. The mechanism causing the L-T coupling in liquid Li at high pressure can be connected to pressure-induced strongly non-

spherical distributions of electron density around ions reported in Ref. 53. The emergence of unusually high-frequency transverse modes was observed only at quite large wave numbers that can be an evidence of their localized nature. It is obvious that in liquids with short-living covalent bonds, like liquid Ga or Sn, there can exist localized excitations with finite lifetime which have analogy with optic-like excitations because of the motion of bonded neighbors with opposite phases. Emergence of this kind of excitations in a liquid alkali metal under high pressure was not expected before. So far, the theory of L and T optic-like excitations was developed only for binary liquids^{68,70} and by date, it is not clear how one can treat theoretically short-time bonded units in dynamical models for pure one-component liquids. One of the possibilities is to treat such a one-component metal as a two-component chemically reacting system.³⁵ The development of the extended dynamical models in this direction together with simulation data can reveal new types of collective excitations in liquids under high pressure.

We proposed a methodology of analysis of transverse dynamics based on extended hydrodynamics that explicitly takes into account frequency moments of $C^T(k, \omega)$ and time moments of the transverse current autocorrelation function. In contrast to the regular viscoelastic model of transverse dynamics, which is unable to correctly describe the AIMD-derived $F_{JJ}^T(k, t)$ at high pressures, the five-variable extended model results in two branches of coupled collective excitations and perfectly reproduces the simulation data. The obtained two branches of eigenvalues show nice agreement with the observed peak positions of the $C^T(k, \omega)$. We stress that the proposed methodology is based on frequency and time moments for only transverse dynamics and does not account explicitly for the cross-correlations between the L and T excitations. This is the first step in theoretical analysis of the transverse dynamics showing the presence of contributions from two propagating modes. Another GCM methodology for explicit treatment of coupled L and T dynamics in liquid metals under pressure will be reported elsewhere.

ACKNOWLEDGMENTS

The computing time allocation for the *ab initio* simulations in frames of the CINECA project “Dynamics and thermodynamics of compressed liquid metals studied by *ab initio* molecular dynamics” is gratefully acknowledged.

We are grateful to L. E. Gonzalez (Valladolid) for providing us with the effective pair potential for liquid Li. The calculations have been performed using the *ab initio* total-energy and molecular dynamics program VASP (Vienna *ab initio* simulation program) developed at the Institute für Materialphysik of the Universität Wien.^{71–73}

¹N. H. March, *Liquid Metals: Concepts and Theory* (Cambridge University Press, 1990).

²T. Scopigno, G. Ruocco, and F. Sette, *Rev. Mod. Phys.* **77**, 881 (2005).

³R. A. MacPhail and D. Kivelson, *J. Chem. Phys.* **80**, 2102 (1984).

⁴T. Bryk and I. Mryglod, *Phys. Rev. E* **62**, 2188 (2000).

⁵L. D. Landau and G. Placzek, *Phys. Z. Sowjetunion* **5**, 172 (1934).

⁶R. D. Mountain, *Rev. Mod. Phys.* **38**, 205 (1966).

⁷N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids* (MacMillan Press, London, 1976).

- ⁸S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter*, International Series of Monographs on Physics (Clarendon Press, Oxford, 1984), Vol. 72.
- ⁹U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).
- ¹⁰J. R. D. Copley and S. W. Lovesey, *Rep. Prog. Phys.* **38**, 461 (1975).
- ¹¹A. Z. Akcasu and E. Daniels, *Phys. Rev. A* **2**, 962 (1970).
- ¹²M. H. Ernst and J. R. Dorfman, *J. Stat. Phys.* **12**, 311 (1975).
- ¹³B. Bagchi and S. Bhattacharyya, "Mode coupling theory approach to the liquid-state dynamics," in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (John Wiley & Sons, New York, 2001), Vol. 116.
- ¹⁴I. M. de Schepper and E. G. D. Cohen, *Phys. Rev. A* **22**, 287 (1980).
- ¹⁵I. M. de Schepper and E. G. D. Cohen, *J. Stat. Phys.* **27**, 223 (1982).
- ¹⁶E. G. D. Cohen, I. M. de Schepper, and M. J. Zuilhof, *Physica B+C* **127**, 282 (1984).
- ¹⁷S. W. Lovesey, *Phys. Rev. Lett.* **53**, 401 (1984).
- ¹⁸T. Bryk and I. Mryglod, *Phys. Rev. E* **64**, 032202 (2001).
- ¹⁹J.-F. Wax and T. Bryk, *J. Phys.: Condens. Matter* **26**, 168002 (2014).
- ²⁰I. M. de Schepper, P. Verkerk, A. A. van Well, and L. A. de Graaf, *Phys. Rev. Lett.* **50**, 974 (1983).
- ²¹L. A. de Graaf and I. M. de Schepper, *J. Phys.: Condens. Matter* **2**, SA99 (1990).
- ²²S. Cazzato, T. Scopigno, T. Bryk, I. Mryglod, and G. Ruocco, *Phys. Rev. B* **77**, 094204 (2008).
- ²³S. Hosokawa, M. Inui, Y. Kajihara, K. Matsuda, T. Ichitsubo, W.-C. Pilgrim, H. Sinn, L. E. Gonzalez, D. J. Gonzalez, S. Tsutsui, and A. Q. R. Baron, *Phys. Rev. Lett.* **102**, 105502 (2009).
- ²⁴V. M. Giordano and G. Monaco, *Proc. Natl. Acad. Sci. U. S. A.* **107**, 21985 (2010).
- ²⁵G. Simeoni, T. Bryk, F. A. Gorelli, M. Krisch, G. Ruocco, M. Santoro, and T. Scopigno, *Nat. Phys.* **6**, 503 (2010); F. A. Gorelli, M. Santoro, T. Scopigno, M. Krisch, and G. Ruocco, *Phys. Rev. Lett.* **97**, 245702 (2006).
- ²⁶V. M. Giordano and G. Monaco, *Phys. Rev. B* **84**, 052201 (2011).
- ²⁷T. Bryk and I. Mryglod, *Chem. Phys. Lett.* **466**, 56 (2008).
- ²⁸T. Bryk, I. Mryglod, T. Scopigno, G. Ruocco, F. Gorelli, and M. Santoro, *J. Chem. Phys.* **133**, 024502 (2010).
- ²⁹T. Bryk and J.-F. Wax, *J. Phys.: Condens. Matter* **24**, 505102 (2012).
- ³⁰T. Bryk and I. Mryglod, *Condens. Matter Phys.* **11**, 139 (2008).
- ³¹T. Bryk and I. Mryglod, *Phys. Rev. B* **79**, 184206 (2009).
- ³²T. Bryk and J.-F. Wax, *Phys. Rev. B* **80**, 184206 (2009).
- ³³F. A. Gorelli, T. Bryk, M. Krisch, G. Ruocco, M. Santoro, and T. Scopigno, *Sci. Rep.* **3**, 1203 (2013).
- ³⁴J.-P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
- ³⁵B. J. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics* (Dover, New York, 2000).
- ³⁶T. Bryk, *Eur. Phys. J.: Spec. Top.* **196**, 65 (2011).
- ³⁷S. Hosokawa, M. Inui, Y. Kajihara, K. Matsuda, T. Ichitsubo, W.-C. Pilgrim, H. Sinn, L. E. Gonzalez, D. J. Gonzalez, S. Tsutsui, and A. Q. R. Baron, *Eur. Phys. J.: Spec. Top.* **196**, 85 (2011).
- ³⁸S. Munejiri, F. Shimojo, and K. Hoshino, *Phys. Rev. B* **86**, 104202 (2012).
- ³⁹S. Hosokawa, S. Munejiri, M. Inui, Y. Kajihara, W.-C. Pilgrim, Y. Ohmasa, S. Tsutsui, A. Q. R. Baron, F. Shimojo, and K. Hoshino, *J. Phys.: Condens. Matter* **25**, 112101 (2013).
- ⁴⁰G. I. A. Stegeman and B. P. Stoicheff, *Phys. Rev. Lett.* **21**, 202 (1968).
- ⁴¹V. Volterra, *Phys. Rev.* **180**, 156 (1969).
- ⁴²N. K. Ailawadi, B. J. Berne, and D. Forster, *Phys. Rev. A* **3**, 1472 (1971).
- ⁴³G. I. A. Stegeman and B. P. Stoicheff, *Phys. Rev. A* **7**, 1160 (1973).
- ⁴⁴M. Sampoli, G. Ruocco, and F. Sette, *Phys. Rev. Lett.* **79**, 1678 (1997).
- ⁴⁵A. Cimattoribus, S. Saccani, F. Bencivenga, A. Gessini, M. G. Izzo, and C. Masciovecchio, *New J. Phys.* **12**, 053008 (2010).
- ⁴⁶J.-Y. Raty, E. Schwegler, and S. A. Bonev, *Nature* **449**, 448 (2007).
- ⁴⁷I. Tamblyn, J.-Y. Raty, and S. A. Bonev, *Phys. Rev. Lett.* **101**, 075703 (2008).
- ⁴⁸J. Yang, J. S. Tse, and T. Iitaka, *J. Chem. Phys.* **135**, 044507 (2011).
- ⁴⁹T. Bryk, S. De Panfilis, F. A. Gorelli, E. Gregoryanz, M. Krisch, G. Ruocco, M. Santoro, T. Scopigno, and A. P. Seitsonen, *Phys. Rev. Lett.* **111**, 077801 (2013).
- ⁵⁰H. K. Mao, J. Xu, V. V. Struzhkin, J. Shu, R. J. Hemley, W. Sturhahn, M. Y. Hu, E. E. Alp, L. Vocadlo, D. Alfé, G. D. Price, M. J. Gillan, M. Schwoerer-Böhning, D. Häusermann, P. Eng, G. Shen, H. Giefers, R. Lübbbers, and G. Wortmann, *Science* **292**, 914 (2001).
- ⁵¹A. Kietzmann, R. Redmer, M. P. Desjarlais, and T. R. Mattsson, *Phys. Rev. Lett.* **101**, 070401 (2008).
- ⁵²M. A. Morales, C. Pierleoni, E. Schwegler, and D. M. Ceperley, *Proc. Natl. Acad. Sci. U. S. A.* **107**, 12799 (2010).
- ⁵³T. Bryk, I. Kleevts, G. Ruocco, T. Scopigno, and A. P. Seitsonen, *Phys. Rev. B* **90**, 014202 (2014).
- ⁵⁴P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ⁵⁵G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ⁵⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁵⁷Ya. Chushak, T. Bryk, A. Baumketner, G. Kahl, and J. Hafner, *Phys. Chem. Liq.* **32**, 87 (1996).
- ⁵⁸T. Bryk and I. Mryglod, *J. Phys.: Condens. Matter* **12**, 3543 (2000).
- ⁵⁹T. Bryk and I. Mryglod, *Phys. Rev. E* **63**, 051202 (2001).
- ⁶⁰I. P. Omelyan and M. V. Tokarchuk, *J. Phys.: Condens. Matter* **12**, L505 (2000).
- ⁶¹I. M. de Schepper, E. G. D. Cohen, C. Bruin, J. C. van Rijs, W. Montfrooij, and L. A. de Graaf, *Phys. Rev. A* **38**, 271 (1988).
- ⁶²I. M. Mryglod, I. P. Omelyan, and M. V. Tokarchuk, *Mol. Phys.* **84**, 235 (1995).
- ⁶³T. Bryk and G. Ruocco, *Mol. Phys.* **111**, 3457 (2013).
- ⁶⁴T. Bryk, I. Mryglod, and G. Kahl, *Phys. Rev. E* **56**, 2903 (1997).
- ⁶⁵J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic, London, 2005).
- ⁶⁶T. Bryk and I. Mryglod, *Phys. Rev. B* **82**, 174205 (2010).
- ⁶⁷A. Alavi, M. Parrinello, and D. Frenkel, *Science* **269**, 1252 (1995).
- ⁶⁸T. Bryk and I. Mryglod, *J. Phys.: Condens. Matter* **12**, 6063 (2000).
- ⁶⁹H. Shintani and H. Tanaka, *Nat. Mater.* **7**, 870 (2008).
- ⁷⁰T. Bryk and I. Mryglod, *J. Phys.: Condens. Matter* **14**, L445 (2002).
- ⁷¹G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); **49**, 14251 (1994).
- ⁷²G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ⁷³G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).