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AB INITIO SIMULATION STUDY OF COLLECTIVE EXCITATIONS IN A MOLECULAR HYDROGEN FLUID

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We report a theoretical analysis of collective dynamics in a molecular Hydrogen fluid performed within a combination of *ab initio* molecular dynamics (AIMD) simulations and the approach of Generalized collective Modes (GCM). A five-variable thermo-viscoelastic model of generalized hydrodynamics was applied to recover four different collective time correlation functions, obtained from AIMD. Dispersion of collective excitations in a molecular Hydrogen fluid, obtained from peak positions of the current spectral functions as well as from the GCM eigenvalues, is reported.

Key words: molecular Hydrogen, collective excitations, generalized hydrodynamics, *ab initio* molecular dynamics.

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I. INTRODUCTION

Collective dynamics in liquids on macroscopic scales in equilibrium can be represented as a collection of hydrodynamic collective modes, which correspond to relaxing and propagating processes reflected solely by fluctuations of conserved quantities. In the case of simple liquids, one has five conserved quantities: number of particles, three components of total momentum, and total energy — hence, the hydrodynamic collective modes in simple liquids can be easily estimated. In longitudinal dynamics, there exist just a pair of acoustic propagating modes propagating adiabatically in opposite directions with linear dispersion law $\omega_s(k)$ plus a heat relaxation mode tending to equalize the difference in local temperatures caused by the adiabatic sound wave [1, 2]. In the transverse case, there are simply two identical shear relaxation modes in two transverse directions. On mesoscopic spatial scales, when the atomistic structure of matter becomes relevant, non-hydrodynamic modes become important in collective dynamics: stress relaxation, structural relaxation, shear and heat waves, optic-like excitations in ionic and many-component liquids, etc. [3, 4]. On mesoscopic and microscopic spatial, scales one needs to apply the methods of generalized hydrodynamics to account for non-hydrodynamic effects in collective dynamics of liquids [1, 5–9].

For the case of molecular liquids, there were several schemes of how to extend hydrodynamic description of collective dynamics to the molecular scale [10–16]. Note that even in the case of water, which is rather a complex molecular polar liquid, the generalized hydrodynamic five-variable thermo-viscoelastic (TVE) description was very reasonable in recovering simulation results on the short-time collective dynamics of water [12, 13], although more precise schemes allowed us to recover the long-time dynamics too [16].

Hydrogen fluid is of special interest because of its great role in green energy production. Many theoretical and simulation studies were dedicated to the structural and dynamic properties of Hydrogen fluid at ambient conditions and high pressures [17–23]. Collective dynamics in molecular Hydrogen fluid is much less studied than that in simple liquids or water. It is not known how the extended hydrodynamic modes behave outside the hydrodynamic regime. The case of collective dynamics in molecular Hydrogen studied by AIMD is even more complicated than that of simple atomic Hydrogen fluids. The vibrational spectrum of molecular Hydrogen will contain high-frequency intramolecular modes. It is unknown how the generalized hydrodynamics and in particular the TVE model will be working in this case.

Therefore, our aim in this study was to apply a method of Generalized Collective Modes (GCM) [7, 8, 24] for the analysis of collective time correlation functions obtained in *ab initio* computer simulations. The remaining paper has the following structure: in the next Section, we provide details of our *ab initio* simulations of molecular Hydrogen fluid and theoretical approach; in Section III, we report our results on the application of the thermo-viscoelastic model to the analysis of collective dynamics in molecular Hydrogen fluid; and the last Section will contain conclusions of this study.

II. *AB INITIO* SIMULATIONS AND THEORETICAL ANALYSIS

We performed *ab initio* simulations of a supercritical molecular Hydrogen fluid at temperature 2500 K and density 284.73 kg/m^3, using a system of 1000 particles (500 molecules) with periodic boundary conditions. The high temperature allowed us to use classical equations of motion for particles, while the electron subsystem was brought to the ground state within the density functional theory (DFT) with exchangecorrelations treated in the generalized gradient approximation (Perdew–Burke–Ernzerhof version) [25]. The estimated pressure at our simulated thermodynamic point was 8.4 GPa. The time step in *ab initio* simulations was 0.2 fs. After an initial equilibration over 2 ps, we performed the production run over the 39 000 timesteps. The temperature control during the simulations was provided by a Nosé–Hoover thermostat as implemented in the VASP package with the mass-parameter $SMASS = 1.0$ [26–29].

We made use of the electron-ion interaction represented by the projector-augmented waves (PAW) potentials [30, 31] as implemented in the VASP package (version PAW_PBE H 15Jun2001). The wave functions were expanded in plane waves with the default cut-off energy of 250 eV. For the construction of electron density, we used only the Γ point in the Brillouin zone. Sixty wave numbers k were sampled in the calculation of the static and time correlation functions. The smallest wave numbers was $k_{\min} = 2\pi/L = 0.349\,\text{Å}^{-1}$, where the actual box length $L = 18.00$ Å was used. The calculated k-dependent static and time correlation functions were averaged over all possible directions of wave vectors having the same absolute value.

During the production run, we sampled spatial Fourier components of number density:

$$n(k,t) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{-i\mathbf{k}\mathbf{r}_j}, \tag{1}$$

longitudinal (L) mass-current density

$$J^{\mathrm{L}}(k,t) = \frac{m}{\sqrt{N}} \sum_{j=1}^{N} \frac{(\mathbf{k}\mathbf{v}_j)}{k} e^{-i\mathbf{k}\mathbf{r}_j}, \tag{2}$$

transverse (T) mass-current density

$$\mathbf{J}^{\mathrm{T}}(k,t) = \frac{m}{\sqrt{N}} \sum_{j=1}^{N} \frac{[\mathbf{k}\mathbf{v}_j]}{k} e^{-i\mathbf{k}\mathbf{r}_j}, \tag{3}$$

and first time derivatives of $\dot{J}^{\mathrm{L}}(k,t)$ and $\dot{\mathbf{J}}^{\mathrm{T}}(k,t)$

$$\frac{dJ^{\mathrm{L}}(k,t)}{dt} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \frac{(\mathbf{k}\mathbf{F}_j) - im(\mathbf{k}\mathbf{v}_j)^2}{k} e^{-i\mathbf{k}\mathbf{r}_j(t)}, \tag{4}$$

$$\frac{d\mathbf{J}^{\mathrm{T}}(k,t)}{dt} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \frac{[\mathbf{k}\mathbf{F}_j] - im[\mathbf{k}\mathbf{v}_j](\mathbf{k}\mathbf{v}_j)}{k} e^{-i\mathbf{k}\mathbf{r}_j(t)}, \tag{5}$$

where m is the atomic mass of Hydrogen, $\mathbf{r}_j(t)$, $\mathbf{v}_j(t)$ and $\mathbf{F}_j(t)$ are the coordinate, velocity, and force acting on the j-th particle. As was discussed in [32, 33], the spatial Fourier components of the energy density are extremely time consuming to sample in DFT in comparison with classical MD simulations with effective interatomic potentials. Therefore, for the generalized hydrodynamic analysis of collective dynamics in connection with *ab initio* simulations, we made use of the GCM approach for one-component liquids suggested in Ref. [32], although another fitting scheme based on GCM representation of *ab initio* time correlation functions [34] is applicable too.

The general scheme of the GCM analysis consists in the estimation of the generalized hydrodynamic matrix $\mathbf{T}(k)$ on a chosen basis set of dynamic variables and calculations of its matrix elements $T_{ij}(k)$. Then one needs to find the eigenvalues and eigenvectors of the constructed generalized hydrodynamic matrix $\mathbf{T}(k)$. The pairs of estimated complex-conjugated eigenvalues correspond to propagating modes, while purely real eigenvalues — to non-propagating relaxation processes. The associated eigenvectors allow one to calculate so-called mode strengths (weights) of the dynamic eigenmodes in relevant time correlation functions or in the dynamic structure factors. In this study, the GCM analysis of MD-derived time correlation functions was performed within the thermo-viscoelastic five-variable dynamic model, which for the case of longitudinal dynamics [7] reads as follows:

$$\mathbf{A}^{(\mathrm{TVE})}(k,t) = \left\{ n(k,t), J^{\mathrm{L}}(k,t), \varepsilon(k,t), \dot{J}^{\mathrm{L}}(k,t), \dot{\varepsilon}(k,t) \right\}, \tag{6}$$

where the dynamic variable of energy current is $\dot{\varepsilon}(k,t)$. The construction of the 5×5 generalized hydrodynamic matrix $\mathbf{T}(k)$ using the set of dynamic variables (6) is performed in the following way [8, 24]

$$\mathbf{T}(k) = \mathbf{F}(k,t=0)\tilde{\mathbf{F}}^{-1}(k,z=0), \tag{7}$$

where the majority of matrix elements of 5×5 matrix of static correlation functions $\mathbf{F}(k,t=0)$ and of the matrix of the Laplace-transformed time correlation functions in Markovian approximation $\tilde{\mathbf{F}}(k,z=0)$ are taken directly from AIMD. The matrix elements which need the knowledge of $\varepsilon(k,t)$ and $\dot{\varepsilon}(k,t)$ are taken as fitting parameters to recover a number of AIMD-derived time correlation functions by their GCM theoretical replicas as was suggested in [32]. In the original scheme in [32], the theoretical GCM replicas were calculated for density-density $F_{nn}(k,t)$ and longitudinal current-current $F_{JJ}^{\mathrm{L}}(k,t)$ time correlation functions, and the number of fitting parameters was 6 to recover these two AIMD-derived functions. In this AIMD study, we additionally will consider another time correlation function $F_{nJ}(k,t)$, the imaginary part of which upon the time Fourier transformation results in the density response function $\chi(k,\omega)$, which is related to the dynamic structure factor as follows:

$$\operatorname{Im}\chi(k,\omega) = \frac{m\omega}{k} S(k,\omega).$$

Also, we will calculate the time correlation function $F_{dJdJ}^{\mathrm{L}}(k,t) = \langle \dot{J}^{\mathrm{L}}(-k,t)\dot{J}^{\mathrm{L}}(k,t=0)\rangle$, the spectral function of which is related to the longitudinal current spectral function in the following way

$$D(k,\omega) = \omega^2 C^{\mathrm{L}}(k,\omega).$$

All the theoretical GCM replicas of time correlation functions between dynamic variables from the TVE set

(6) are represented via separable contributions from dynamic eigenmodes [8, 35]:

$$F_{ij}(k,t)=\sum_{\alpha=1}^{N_v} G_{ij}(k)e^{-z_\alpha(k)t}, \tag{8}$$

where $z_\alpha(k)$ is the α-th real (relaxing mode) or complex (propagating) eigenmode, and the weight coefficients of each mode contribution $G_{ij}(k)$ are expressed via associated eigenvectors [8]. We will use expression (8) for the comparison of the AIMD derived time correlation functions with their GCM replicas.

For the analysis of collective dynamics, the adiabatic speed of sound c_s is needed. This quantity is a characteristic of sound propagation in the macroscopic hydrodynamic regime. Another quantity, the high-frequency speed of sound c_∞, reflects the elastic mechanism of sound propagation. The macroscopic adiabatic speed of sound was calculated by using the methodology suggested in [36] as

$$c_\mathrm{s}=\sqrt{c_\infty^2-\psi^\mathrm{L}(0)/\rho}, \tag{9}$$

where $\psi^\mathrm{L}(0)$ is the value of the static correlations for diagonal components of the stress tensor $\psi^\mathrm{L}(0) = V\langle\bar\sigma_{zz}\bar\sigma_{zz}\rangle/k_\mathrm{B}T$, where $\bar\sigma_{zz}(t)=\sigma_{zz}(t)-P$ is the fluctuating part of the diagonal component of the stress tensor and P is the pressure, and V is the volume of the simulated system, and k_B is the Boltzmann constant. The high-frequency speed of sound c_∞ in (9) was estimated from the long-wavelength asymptote of a wavenumber-dependent quantity (normalized second frequency moments of the current spectra function):

$$c_\infty \overset{k\to 0}{=} \frac{1}{k}\left[\frac{\langle \dot J^\mathrm{L}(-k)\dot J^\mathrm{L}(k)\rangle}{\langle J^\mathrm{L}(-k)J^\mathrm{L}(k)\rangle}\right]^{1/2}. \tag{10}$$

Similarly, for the transverse case, the speed of non-damped ("bare") transverse excitations c_T was calculated

$$c_T \overset{k\to 0}{=} \frac{1}{k}\left[\frac{\langle \dot{\mathbf{J}}^\mathrm{T}(-k)\dot{\mathbf{J}}^\mathrm{T}(k)\rangle}{\langle \mathbf{J}^\mathrm{T}(-k)\mathbf{J}^\mathrm{T}(k)\rangle}\right]^{1/2}. \tag{11}$$

III. RESULTS AND DISCUSSION

The standard static structural properties of any liquid are its pair distribution function $g(r)$ and static structure factor $S(k)$. The results for these structural functions obtained from AIMD of the molecular Hydrogen fluid are shown in Fig. 1. The pair distribution function obtained in our AIMD has a well-pronounced intramolecular peak centered at $R=0.75\,\text{Å}$, which is in agreement with the intramolecular distance known from experiments [37]. The intermolecular peaks of $g(r)$ are not well pronounced as is typical for low-density fluids. The static structure factor $S(k)$, obtained in AIMD in the sampled range of wave numbers and calculated as instantaneous density-density correlations, shows the main peak at $k_p=3.12\,\text{Å}^{-1}$. The location of the main peak defines the first pseudo-Brillouin zone (Debye wave number) to be at $k_\mathrm{D}=k_p/2$.

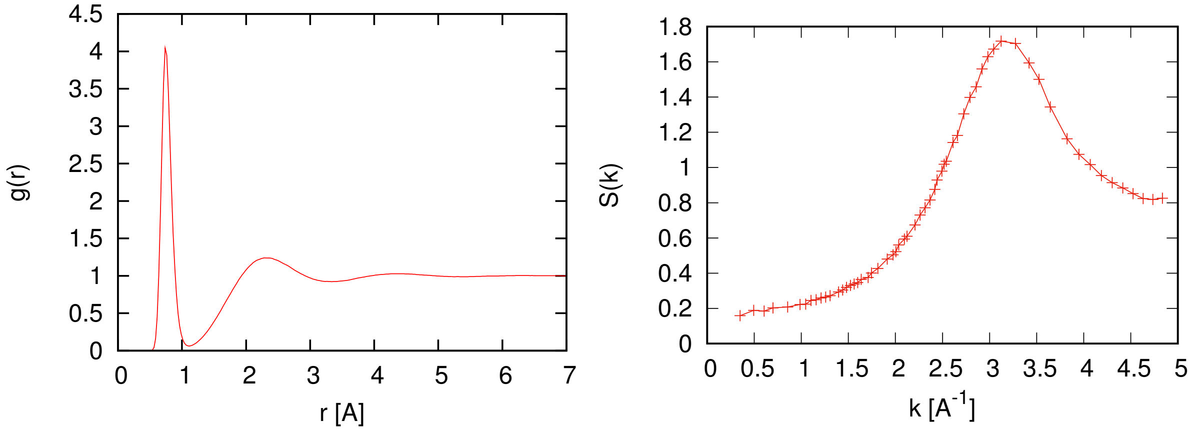

Fig. 1. Pair distribution function $g(r)$ and static structure factor $S(k)$ for molecular Hydrogen at density 284.73 kg/m^3 and temperature 2500 K, obtained from *ab initio* simulations

The single-particle time-dependent properties are represented in Fig. 2 by the normalized velocity autocorrelation function (VACF) and its Fourier spectrum. For molecular Hydrogen, the VACF in Fig. 2 contains fast changes due to the intramolecular normal modes. These normal modes are clearly seen in Fig. 2 having the frequencies between 550 and 900 ps^{-1}. The observed split in the vibrational density of states is due to the coupling with rotational motion as was discussed in [38].

The issue of recovering the collective time correlation functions for molecular Hydrogen by generalized hydrodynamics was studied here by the application of the GCM methodology within the thermo-viscoelastic model (6). The number of dynamic eigenmodes and separable contributions in Eq. (8) in our theoretical analysis was five, and for any wave number, we obtained in this study two pairs of complex-conjugated eigenvalues plus a single real one. In Fig. 3, we show how the GCM theory is able to recover four different AIMD derived time correlation functions. In general, there is good agreement between the AIMD and GCM theory, and what is important, the fast intramolecular oscillations are well recovered as is seen for the function $F_{dJdJ}(k,t)$, which, according to Eq. (4), explicitly accounts for microscopic forces acting on protons.

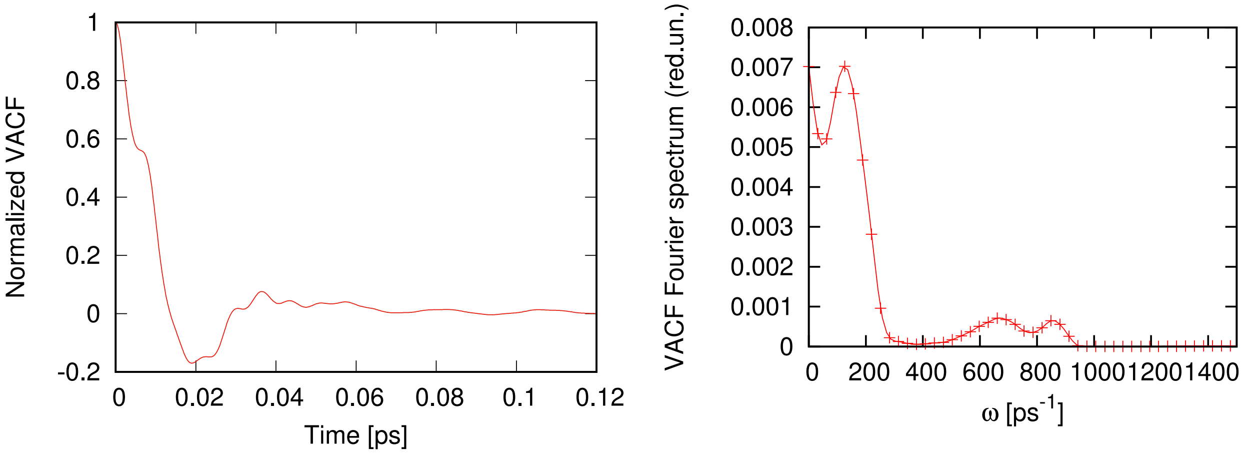

Fig. 2. Normalized velocity autocorrelation function and its Fourier spectrum for molecular Hydrogen at density 284.73 kg/m^3 and temperature 2500 K

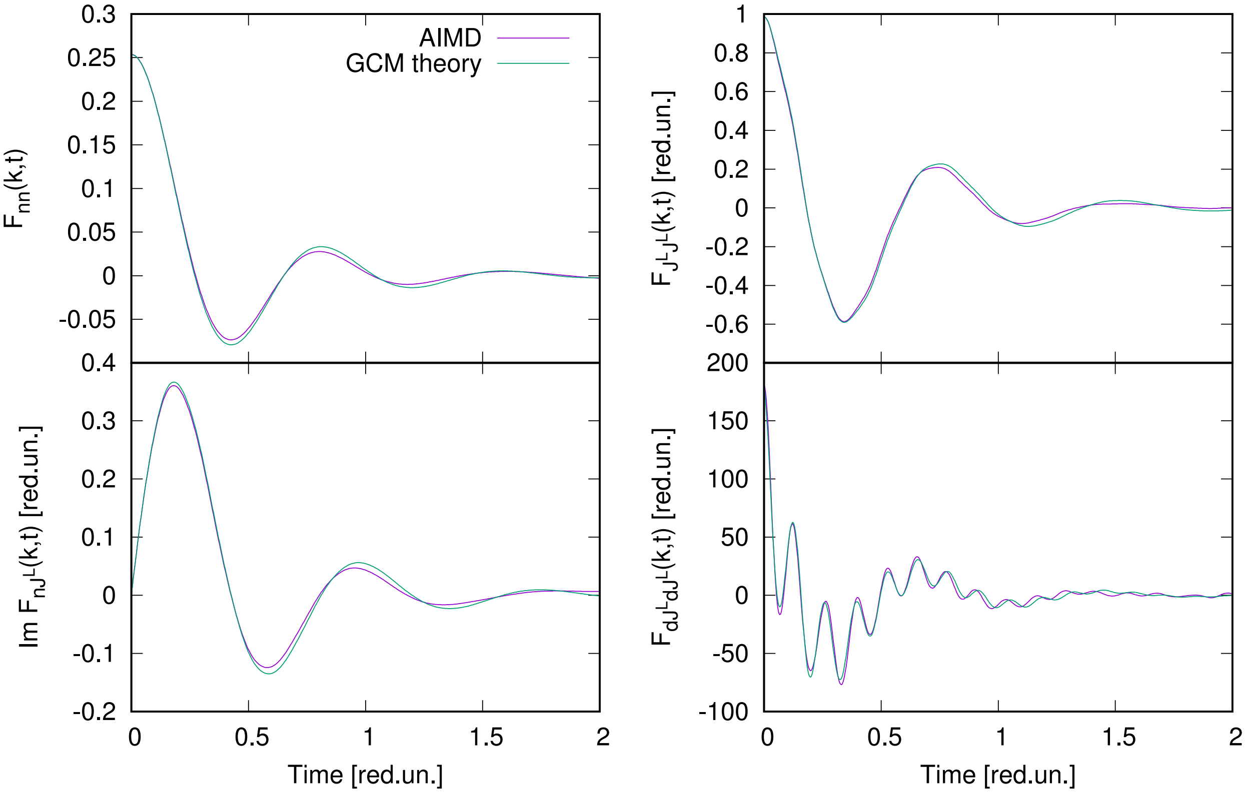

Fig. 3. Recovery of the AIMD-derived time correlation functions by the GCM theory at $k = 1.209\,\text{Å}^{-1}$. $F_{nn}(k,t)$ — density-density correlations, $\text{Im}F_{nJ^\text{L}}(k,t)$ — imaginary part of density response function in time domain, $F_{J^\text{L}J^\text{L}}(k,t)$ — longitudinal current-current correlations, $F_{dJ^\text{L}dJ^\text{L}}(k,t)$ — longitudinal $\langle \dot{J}^\text{L}(-k,t)\dot{J}^\text{L}(k,t=0)\rangle$ correlations

The good recovery of AIMD-derived time correlation functions should result in the same level of precision to describe the corresponding spectral functions. The standard numerical method of estimating of the dispersion of collective excitations from computer simulations consists in following the peak locations in the L and T current spectral functions $C^{\text{L/T}}(k,\omega)$. Here we show in Fig. 4 that the GCM methodology allows nice recovery of the longitudinal current spectral function $C^\text{L}(k,\omega)$ calculated (via numerical Fourier transformation) in the whole range of frequencies, including the part of intramolecular vibrations (the inset in Fig. 4).

The dispersion of longitudinal excitations, obtained via the peak positions of $C^{\mathrm{L}}(k,\omega)$, is shown in Fig. 5. Two well-defined peaks were observed in the shape of the AIMD-derived $C^{\mathrm{L}}(k,\omega)$ at any wave number: the low-frequency peak resulted in the frequencies of extended acoustic excitations, while the dispersionless branch — in the local intramolecular vibrations. In Fig. 5,b one can observe that the dispersion of the acoustic modes has a minimum at k_p — the location of the main peak position of the static structure factor $S(k)$, which corresponds to the second pseudo-Brillouin zone, while at $k_{\mathrm{D}} = k_p/2$ we observe a maximum in the low-frequency dispersion branch. For the transverse case, we did not observe the low-frequency peak of $C^{\mathrm{T}}(k,\omega)$, which would indicate the existing shear waves in molecular Hydrogen fluid.

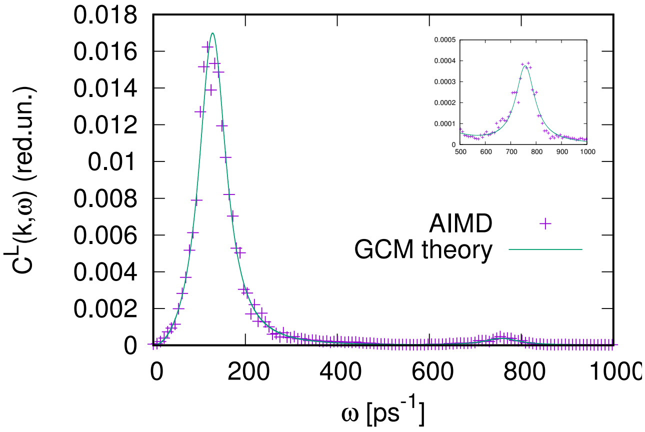

Fig. 4. Recovery of the AIMD-derived longitudinal current spectral function $C^{\mathrm{L}}(k,\omega)$ by the GCM theory at $k = 1.209\,\text{Å}^{-1}$. The inset shows the high-frequency peak of intramolecular vibrations on a larger scale

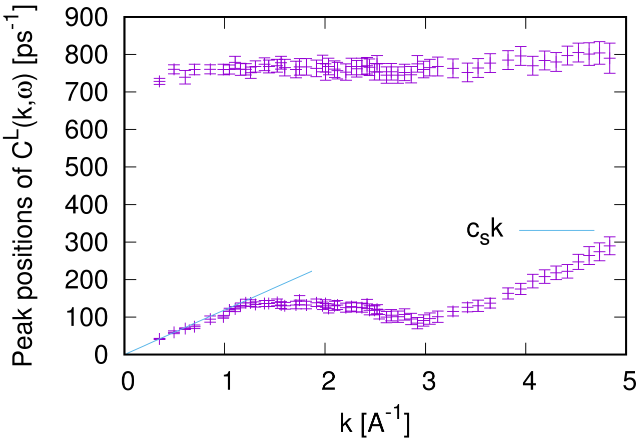

Fig. 5. Peak positions of the AIMD-derived longitudinal current spectral function $C^{\mathrm{L}}(k,\omega)$. The straight line corresponds to the hydrodynamic dispersion law, with the adiabatic speed of sound estimated in this study by using Eq. (9)

The straight line in Fig. 5 corresponds to the hydrodynamic linear dispersion law, with c_{s} being the adiabatic speed of sound. One can see that the linear dispersion perfectly matches the dispersion curve of acoustic modes. The value c_{s} was obtained by using Eq. (9), which needs the values of the high-frequency speed of sound c_∞ and of the instantaneous correlations of diagonal components of the stress tensor. The latter was obtained from our AIMD simulations as $\psi^{\mathrm{L}}(0) = 65.83$ GPa, while the former was obtained from the long-wavelength asymptote of Eq. (10) (as is shown in Fig. 6). The high-frequency speed was obtained $c_\infty = 19313.20$ m/s, while Eq. (9) resulted in the adiabatic speed of sound $c_{\mathrm{s}} = 11907.99$ m/s. For comparison, in Fig. 6 we also show the wave number dependence of the normalized second frequency moment of the transverse current spectral function, estimated from AIMD simulations, which enabled us to estimate according to Eq. (11) the speed of non-damped ("bare") long-wavelength transverse modes $c_{\mathrm{T}} = 11440.0$ m/s.

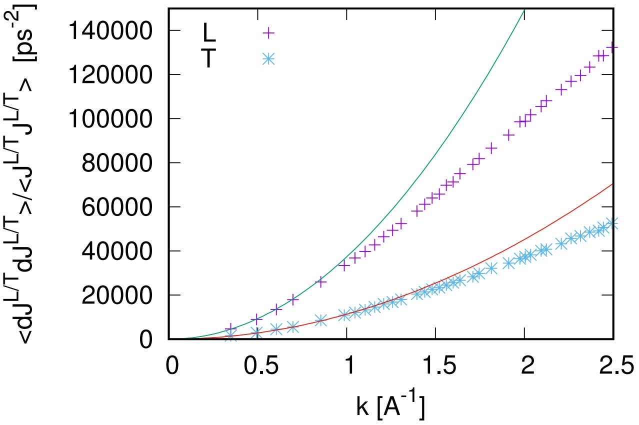

Fig. 6. Wave-number dependence of the static $\langle \dot{J}^{\mathrm{L/T}}(-k)\dot{J}^{\mathrm{L/T}}(k)\rangle / \langle J^{\mathrm{L/T}}(-k)J^{\mathrm{L/T}}(k)\rangle$ correlations for the longitudinal (L) and transverse (T) case and evidence of their $\sim k^2$ long-wavelength asymptotics

The complex-conjugated GCM acoustic eigenvalues can be represented in the form [7, 8]

$$z_s(k) = \sigma_s(k) \pm i\omega_s(k),$$

where the real part corresponds to the k-dependent damping, while the imaginary part — to the dispersion law. We show the sound eigenvalues in the first pseudo-Brillouin zone in Fig. 7 in comparison with the AIMD-derived peak positions of the longitudinal current spectral function $C^{\mathrm{L}}(k,\omega)$. Also, in Fig. 7 we show the hydrodynamic behavior of dispersion and damping, where the latter should follow the Γk^2 dependence, and in Fig. 7 one can see how the damping corresponds to the hydrodynamic law with the damping coefficient $\Gamma = 34\ \text{Å}^2/ps$. In general, the GCM results show that the TVE model of GCM methodology correctly describes the generalized acoustic modes in the first pseudo-Brillouin zone.

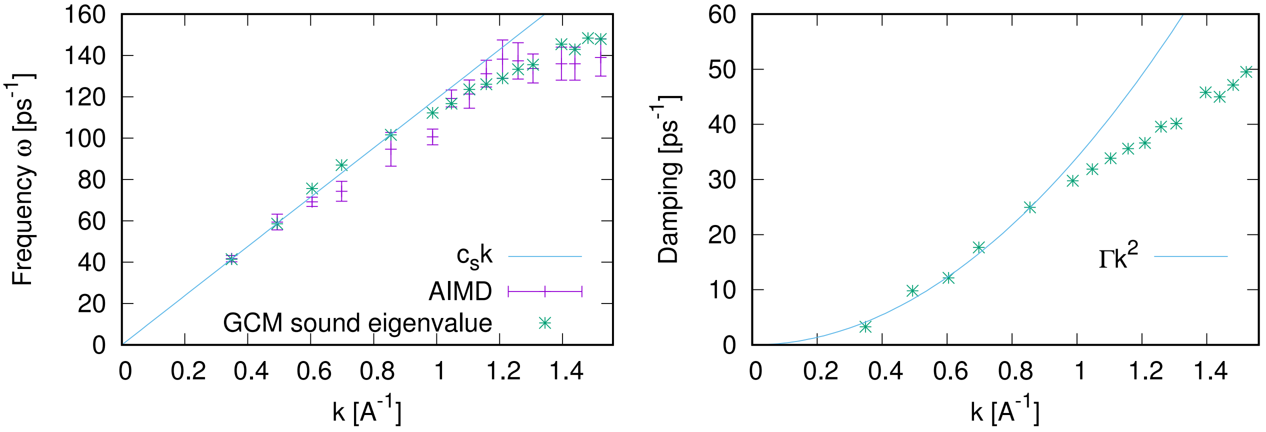

Fig. 7. Dispersion $\omega_s(k)$ as the imaginary part and damping $\sigma_s(k)$ as the real part of GCM complex eigenvalues ('star' symbols) corresponding to extended acoustic excitations in the first pseudo-Brillouin zone. AIMD results from peak positions of $C^{\mathrm{L}}(k,\omega)$ are shown by 'plus' symbols with error bars. The lines correspond to the hydrodynamic dispersion law $c_{\mathrm{s}}k$ and dispersion Γk^2

IV. CONCLUSIONS

We performed *ab initio* molecular dynamics simulations for molecular Hydrogen fluid with the main purpose to analyze its collective dynamics by using the GCM methodology. The case of molecular fluids with intramolecular vibrations was not studied before by using the GCM method, therefore, it was necessary to make sure that some dynamic models within the GCM approach enable correct description of collective modes. Our conclusions of this study are as follows:

i. We applied a five-variable thermo-viscoelastic dynamic model to analyze of AIMD-derived time correlation functions and proved that the GCM eigenvalues correctly recover the dispersion of acoustic modes, as well as they also correspond to the high-frequency branch of intramolecular vibrations;

ii. A new feature in our methodology is that we required recovery of the four AIMD-derived time correlation functions: $F_{nn}(k,t)$, $\mathrm{Im}F_{nJ^{\mathrm{L}}}(k,t)$, $F^{\mathrm{L}}_{JJ}(k,t)$ and $F^{\mathrm{L}}_{dJdJ}(k,t)$ with only 6 (the same number as in the original formulation of the GCM for *ab initio* simulations in [32]) unknown correlators involving energy density and its first time derivative in the generalized hydrodynamic matrix $\mathbf{T}(k)$. Specifically, the microscopic forces which are present in the expression for $F^{\mathrm{L}}_{dJdJ}(k,t)$ enabled nice recovery of the high-frequency dynamics in the molecular Hydrogen fluid;

iii. The methodology for the estimation of the macroscopic adiabatic speed of sound suggested in [36] works fairly well for the case of the molecular Hydrogen fluid. The linear dispersion law with the calculated value of the adiabatic speed of sound $c_{\mathrm{s}} = 11907.99$ m/s perfectly matches AIMD and GCM dispersion curves in the long-wavelength region.

It is very promising to apply the developed methodology of the analysis of collective dynamics to molecular fluids under high pressure. However, this cannot be performed in a straightforward way in the case when Hydrogen molecules break up due to applied pressure. Such systems should be treated as binary ones composed of molecular and atomic units [39]. Hence, the proposed in this study GCM methodology for a fluid of flexible molecules should be extended to binary liquids in a similar way as it was reported recently having a case study of molten NaCl [33].

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ДОСЛІДЖЕННЯ КОЛЕКТИВНИХ ЗБУДЖЕНЬ У МОЛЕКУЛЯРНОМУ ВОДНЕВОМУ ФЛЮЇДІ МЕТОДОМ *AB INITIO*-МОДЕЛЮВАННЯ

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За допомогою комбінації моделювання методом *ab initio* молекулярної динаміки (АІМД) та підходу узагальнених колективних мод (УКМ) зроблено теоретичний аналіз колективної динаміки в молекулярному водневому флюїді. П’ятизмінна термо-в’язкопружна модель узагальненої гідродинаміки була застосована для відтворення чотирьох різних часових кореляційних функцій, отриманих з АІМД. Порівнюємо дисперсію колективних збуджень у молекулярному водневому флюїді, отриману з положень максимумів спектральних функцій потоку та з власних значень узагальненої гідродинамічної матриці підходу УКМ.

Ключові слова: пружні властивості, молекулярні рідини, поширення звуку, *ab initio* молекулярна динаміка.