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Collective Dynamics of Liquid Hg at 523 K

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ABSTRACT

The study presents predictions for the coherent dynamical structure factor $S(k,\omega)$ of liquid mercury (Hg) at 523 K with a density of 12.98 g/cm³. The theoretical results for detailed $S(k,\omega)$ have been reported in the wave-vector, κ range, 0.9 Å⁻¹ to 4.6 Å⁻¹, using the modified microscopic theory of the collective dynamics of a simple liquid. In addition to the structure factor, the study also reports the dispersion relation, sound velocity, and diffusion coefficient for liquid mercury at this temperature and density condition and in this wave vector range. The dynamical structure factors predicted by this theory satisfy significant sum rules relevant to liquids and have an edge over microscopic theory by Hubbard-Beeby (HB) ensuring the consistency and physical validity of the model. Comparison of $S(k,\omega)$ obtained from present modified theory and from microscopic (HB) theory has been made for smaller κ values. The results obtained from present theory are much more realistic as compared to the later theory.

KEYWORDS: Dynamical structure factor, Modified microscopic theory, Current-current correlation function, Collective dynamics, Diffusion coefficient.

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1. INTRODUCTION

The coherent dynamical structure factor, which describes the momentum transfer and the energy exchange between external probe and the system, is the space-time Fourier transform of the van Hove space-time dependent correlation function [1]. This function is a time-extended version of the static pair correlation function and offers detailed insight into the equilibrium dynamics of a system, regardless of whether the system exhibits lattice translational invariance (such as in crystals, disordered solids, or fluids). The dynamics of an interacting fluid is complex due to its disordered and correlated structure, involving both single-particle and collective motions. Despite this complexity, the fluid may exhibit well-defined collective modes that can be directly investigated through experimental techniques like thermal neutron inelastic scattering and inelastic X-ray scattering. However, these methods suffer from certain limitations. Due to significant incoherent scattering induced by neutron-nucleus interactions, it is difficult to isolate the coherent dynamical structure component from inelastic neutron scattering data. In contrast, inelastic X-ray scattering performed using highly resolved synchrotron radiation sources, can yield pure coherent structures, offering a clearer view of the liquid dynamics. These experimentally measured scattering cross-sections are related to the dynamical structure factors which can provide insight to the equilibrium dynamics. These structural functions are correlation functions which can reveal the presence of collective dynamics and can quantize the collective modes through their structures. A few inelastic X-ray scattering (IXS) experiments using high resolution high-flux X-rays from synchrotron sources, have been performed to report coherent $S(\kappa, \omega)$ of liquid Hg at 293 K [2-3] and of gaseous Hg at rarer densities of 1.0, 2.0 and 3.1 gcm^{-3}. [4] While the IXS experiment for liquid Hg accurately provided the $S(k, \omega)$ in huge momentum transfer region 0.3 Å^{-1} ≤ κ ≤ 3.71 Å^{-1} prevalent to two peaks of the static structure factor, in the case of Hg vapour dynamical structure factors for only a few (four) wave-vector values have been measured. Though, some of neutron scattering studies [5-6] have also been reported for liquid Hg, but these are unable to provide pure coherent spectral information. The intermediate temperature range of liquid Hg however is unreported and collective dynamics in this region of the liquid-vapour curve have not been measured through by the IXS experiments.

In the present study, collective dynamics of liquid Hg at 523 K comprising 12.98grams in one cubic centimetres, has been evaluated. The present predictions are based on the modified microscopic theory wherein microscopic behaviour of any condensed system is worked out to yield the density response function. This complex function, comprises an imaginary and a real part, describes the

space-time-dependant fluctuations in the density of any fluid in response to a weak perturbation. When Fourier transformed, the imaginary part of the transformed function is related to the dynamical structure factor, through fluctuation dissipation theorem, which is the most significant correlation function in this study. To incorporate inter-particle correlations which were not included in the previous theory [7], a characteristic relaxation time is introduced [8], which depends on various physical factors, including the static structure factor, density, temperature, mass, interaction potential, and diffusion coefficient. In this theory, the diffusion coefficient is generalized to be wave-vector dependent, with a specific value assigned to each wave-vector. This modification reduces the number of arbitrary parameters and provides a more accurate representation of the intermediate self-scattering function. The revised model has been successfully applied to describe the collective dynamics of several liquids. [9-14]

In this work, the same modified microscopic theory is used to predict the collective dynamics of liquid Hg at 523 K, aiming to explain its response to external radiation and to calculate the dynamical structure factor for liquid Hg.

2. MATHEMATICAL FORMALISM

Microscopic theory solves the microdynamics of any fluid to describes the density fluctuations and depict the courses of moving particles. For further understanding intricate space-time dependant correlation functions are defined which then are approximated to attain results for the dynamical structure factor. During the evolution of the theory and in the evaluation of the dynamical structure factors in the microscopic theory, the distinct time correlations were not taken in to account. The outcomes for the dynamical structure factors generated, hence, were rather damped and were not in the agreement to the experimentally observed spectral lineshapes. The theory is modified, therefore, by Tewari et al. 8 including the neglected correlations for which a characteristic relaxation time is introduced. This form of the modified microscopic theory has successfully explained the dynamical structure factors for several liquids [15-18].

The dynamical structure factor in this is aquires the following form:

$$S(k,\omega) = \frac{k^2}{\pi m \beta}\left\{\left[1+\omega_k^{\ 2}\frac{(\beta''+\gamma)^2-\omega^2}{\left[(\beta''+\gamma)^2+\omega^2\right]^2}\right]\frac{2\beta''}{(\beta''^2+\omega^2)^2}-\omega_k^{\ 2}\frac{(\beta''^2-\omega^2)}{(\beta''^2+\omega^2)^2}\frac{2(\beta''+\gamma)}{\left[(\beta''+\gamma)^2+\omega^2\right]^2}\right\}$$

$$\times\left\{\left[1+\omega_k^{\ 2}\frac{(\beta''+\gamma)^2-\omega^2}{\left[(\beta''+\gamma)^2+\omega^2\right]^2}\right]^2+\left[\omega_k^{\ 2}\frac{2\omega(\beta''+\gamma)}{\left[(\beta''+\gamma)^2+\omega^2\right]^2}\right]^2\right\}^{-1}$$

(1)

In the expression (1), $\beta'' = D_{eff}\kappa^2$, D_{eff} is ω–dependant diffusion coefficient, and $\beta=(k_BT)^{-1}$.

And, $\Upsilon = \tau(\kappa)^{-1}$, $\tau(\kappa)$ is the relaxation time defined in the present theory as follows:

$$[\tau(\kappa)]^{-1}=\frac{\omega_\kappa}{\left[(\kappa^2/m\beta\,S(\kappa)\beta'^2)-1\right]^{1/2}}-\beta'$$

(2)

In the expression (2) $\beta' = D\kappa^2$, D is the diffusion coefficient that varies with κ, m is the atomic mass and $S(\kappa)$ is the static structure factor can be obtained from the Fourier transform of the $g(r)$ as follows:

$$S(\kappa)=1+4\pi\rho_0\int_0^\infty r^2(g(r)-1)\frac{\sin\kappa r}{\kappa r}\,dr$$

(3)

The frequency ω_κ occurred in the expression (1) and (2) is given as follows:

$$\omega_\kappa^{\ 2}=\omega_E^{\ 2}\left[1-\frac{3\sin\kappa r_0}{\kappa r_0}-\frac{6\cos\kappa r_0}{(\kappa r_0)^2}+\frac{6\sin\kappa r_0}{(\kappa r_0)^3}\right]$$

(4)

Here, $V(r)$ is the inter-atomic potential $g(r)$ is the static pair correlation function and z is the space coordinate.

The elastic frequency ω_E and r_0 occurred in the expression (2) are given respectively, as:

$$\omega_E^{\ 2}=\frac{4\pi\rho_0}{3m}\int\left(\frac{\partial^2 V}{\partial r^2}+\frac{2}{r}\frac{\partial V}{\partial r}\right)g(r)r^2dr$$

(5)

And peak $r=r_0$ of the delta function

$$\frac{\partial^2 V}{\partial z^2}g(r)=A\delta(r-r_0)$$

(6)

The current-current correlation function $C(\kappa,\omega)$ is given as follows:

$$C(\kappa,\omega) = \frac{\omega^2}{\kappa^2}S(\kappa,\omega)$$

(7)

3. RESULTS AND DISCUSSION

As suggested by the mathematical section, modified microscopic theory requires knowledge of inter-particle interaction potential for further evolution of dynamics study. A few attempts to generate interparticle interaction potential of Hg in different phases have been made. In gaseous Hg, due to the presence of uncharged atoms, interaction potential comprises a hard core repulsive part along with an attractive part of van der waal's form [19], whereas the liquid state of Hg contains loosely bound electrons with Hg ions, resulted in the presence of long range oscillatory attractive part [20]. The repulsive part of liquid Hg, however, is of the usual hard core form. The considered system of Hg atoms, subject to the physical conditions of 523 K temperature (and density of 12.98 g/cc), however, is essentially a state along liquid-vapour co-existence curve. An interaction potential that is suggested by Stefanov etal. [21],which id determined by distinct physical quantities along liquid-vapour curve, therefore, has been used in the present work. This potential is quite different from the L-J [19] form of potential for gaseous Hg that is applicable in the case of inert gas atoms. Further, the potential has successfully reproduced the experimentally measured static structure factor [20] also.

The interaction potential is when substituted in expression (5) yields the maximum Einstein frequency ω_E and r_0 for liquid Hg that turn out to be 7.116×10^{12} s^{-1} and 2.76 Å, respectively. The experimentally measured static pair correlation function $g(r)$ reported by Inui et al. [22] and also reproduced using this potential form for Hg [20], has been used here. These two entities are further substituted into expression (4) to evaluate ω_κ. The static structure factor $S(\kappa)$ which is evaluated by the Fourier transform of static pair correlation function $g(r)$ using expression (3) along with the evaluated ω_κ are collectively substituted in the expression (3) to provide the characteristic relaxation time $\tau(\kappa)$ that has been introduced in the modified microscopic theory to incorporate distinct correlations, for different values of wave-vector, κ. The diffusion coefficient, D, occurring in the expression (3) has appeared as an arbitrary parameter to satisfy the zeroth sum rule for a given value of wave-vector κ. The detailed dynamical structure factors can now be calculated using expression (1).
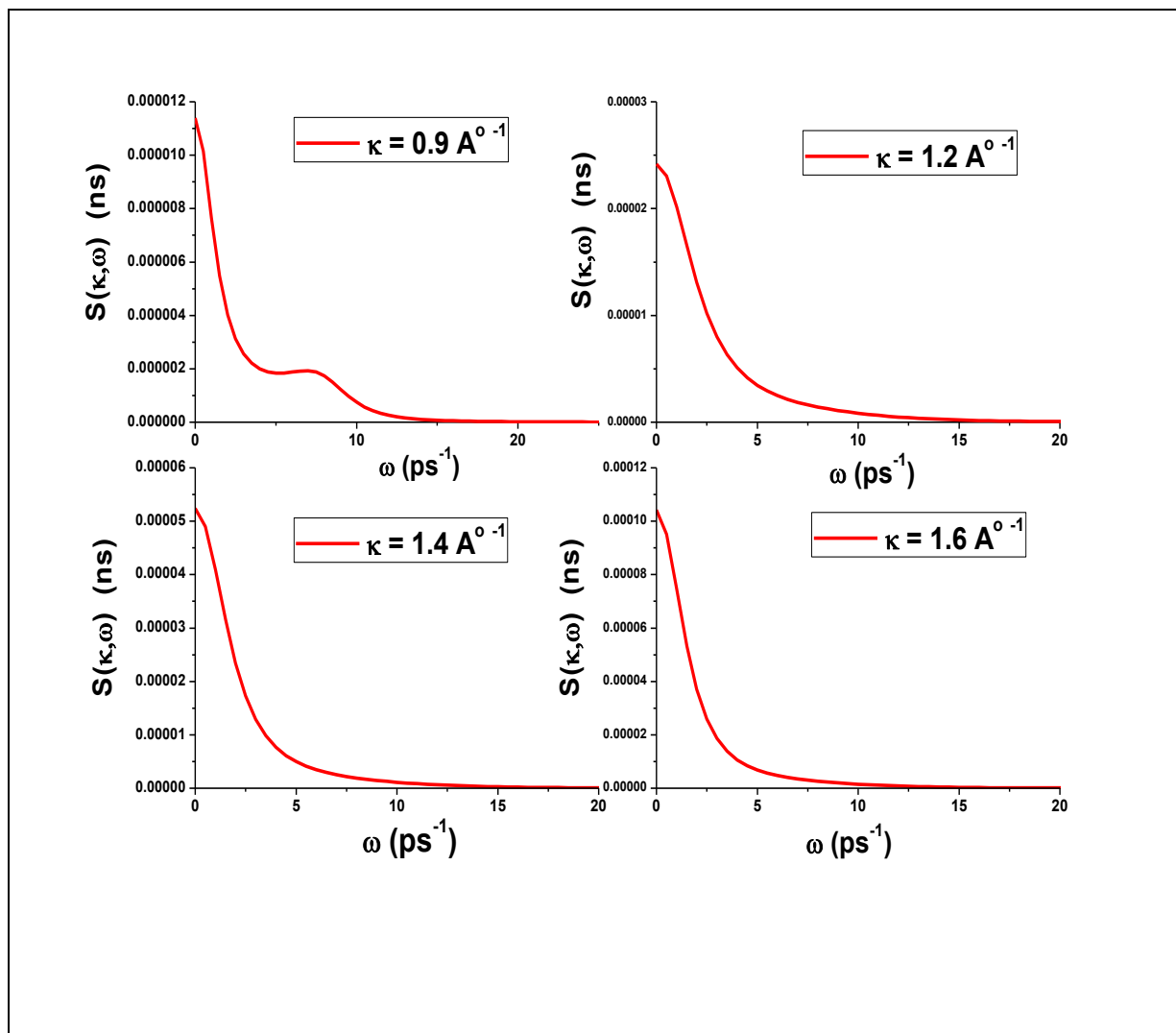
Figure 1: Variation of the dynamical structure factor, $S(\kappa,\omega)$ **of liquid mercury at 523 K with frequency,** ω **: (——)**

at $\kappa = 0.9$ **Å**$^{-1}$, $\kappa = 1.2$ **Å**$^{-1}$, $\kappa = 1.4$ **Å**$^{-1}$ **and** $\kappa = 1.6$ **Å**$^{-1}$.

The dynamical structure factors were calculated using expression (1) for different wave-vector values, spanning a wide range from 0.9 Å$^{-1} \leq \kappa \leq$ 4.6 Å^{-1}. The results, showing how the structure factors vary with frequency, are presented in three figures: Figure 1: $\kappa = 0.9$ Å^{-1}; $\kappa = 1.2$ Å^{-1}; $\kappa = 1.4$ Å^{-1} and $\kappa = 1.6$ Å^{-1} with solid curve (——); Figure 2: $\kappa = 1.8$ Å^{-1}; $\kappa = 2.0$ Å^{-1}; $\kappa = 2.4$ Å^{-1} and $\kappa = 2.7$ Å^{-1} with solid curve (——) and Figure 3: $\kappa = 3.0$ Å^{-1}; $\kappa = 3.5$ Å^{-1}; $\kappa = 4.0$ Å^{-1} and $\kappa = 4.3$ Å^{-1} and $\kappa = 4.6$ Å^{-1} with solid curve (——).
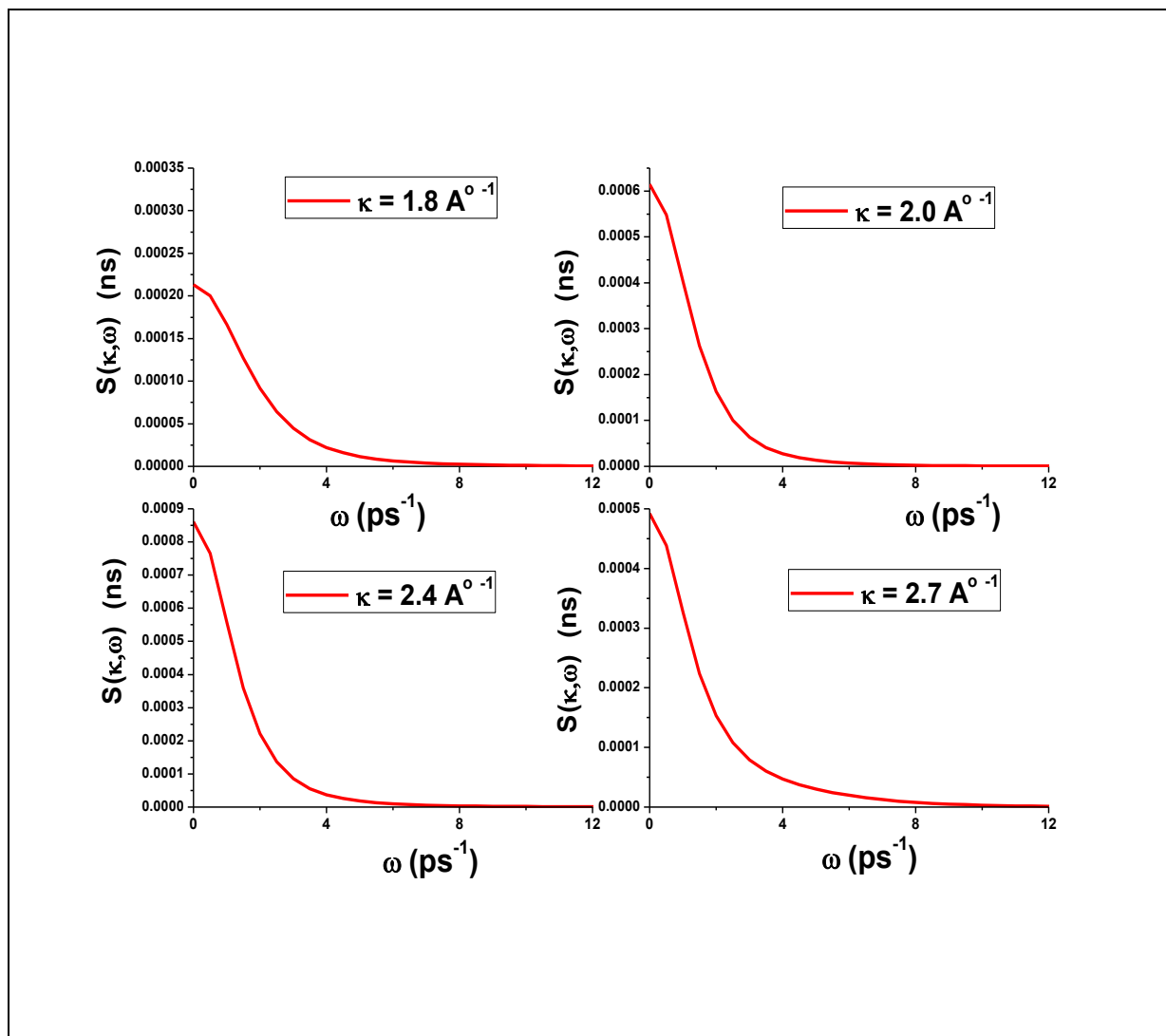
Figure 2: Variation of the dynamical structure factor, $S\left(\kappa,\omega\right)$ **of liquid mercury at 523 K with frequency,** ω **: (———)**

at κ **= 1.8 Å⁻¹ ,** κ **= 2.0 Å⁻¹ ,** κ **= 2.4 Å⁻¹ and** κ **=2.7 Å⁻¹.**

In these calculations, the effective diffusion coefficient, D_{eff} has not been varied with frequency and is same as the diffusion coefficient given in expression (2). As s evident from three Figures , at higher wave-vectors, the dynamical structure factors appear damped and exhibit structures without Brillouin peaks except at 0.9 Å^{-1} . This trend of variation when compared to the liquid Hg at 293 K, are found in sync with the experimentally measured data via Inelastic X-ray Scattering (IXS) 17 of later consideration where prominent side peaks has been observed up to κ =0.8 Å^{-}1 and for also a subdued Brillouin peak in dynamical structure factor has appeared.
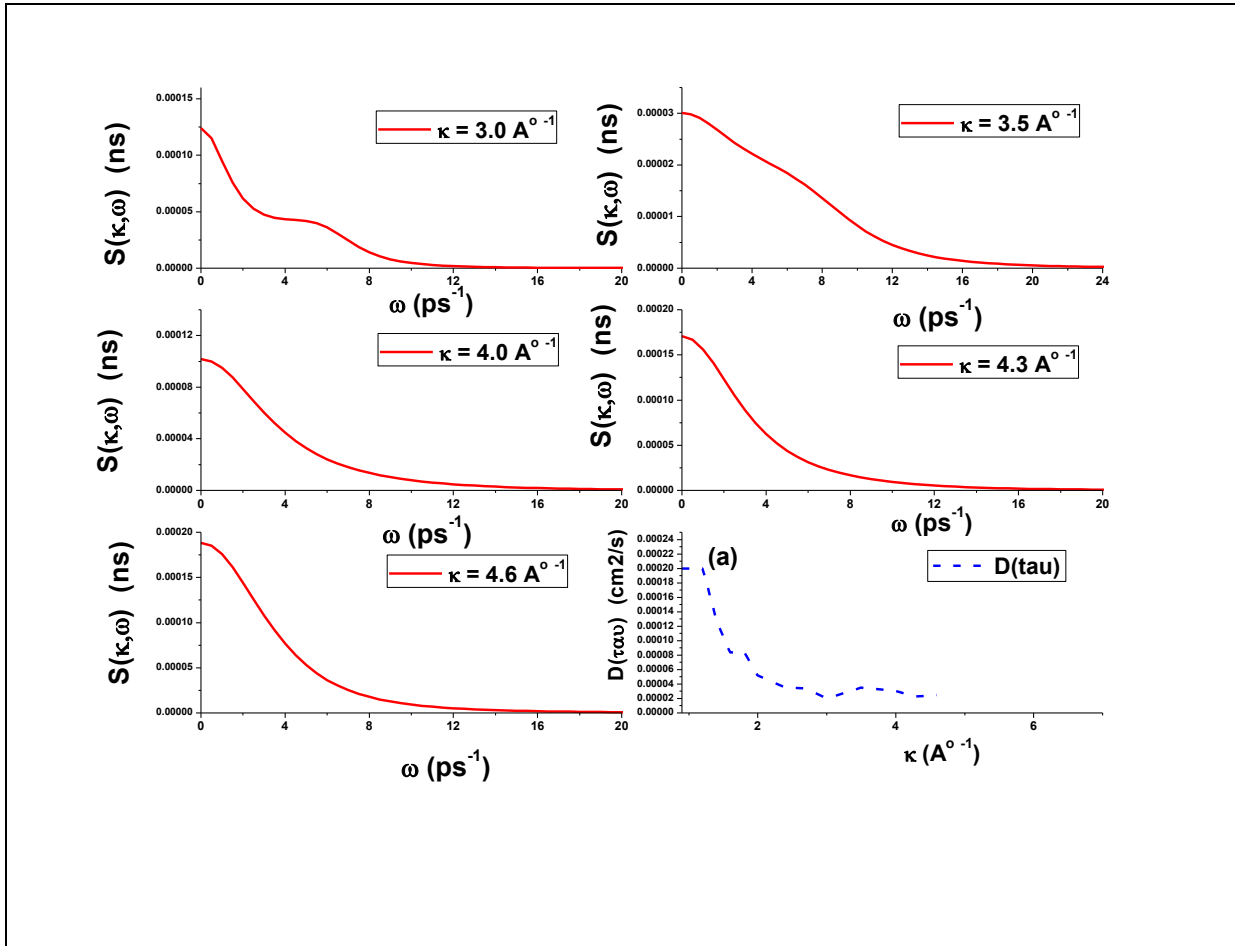

Figure 3: Variation of the dynamical structure factor, $S(\kappa, \omega)$ of liquid mercury at 523 K with frequency, ω : (——) **at κ =3.0 Å^{-1} , κ = 3.5 Å^{-1} , κ = 4.0 Å^{-1}, κ =4.3 Å^{-1} and κ =4.6 Å^{-1}.**

Figure 3(a): Variation of the diffusion co-efficient with wave-vector κ : with (- - -).

The attained results for the self-Diffusion coefficient that serves as a fitting parameter of the theory have been plotted in Figure 2(a) against wave-vector k : with dashed curve (- - -).The obtained values of the diffusion coefficient have been shown in Figure 2(a) as against wave-vector k : with dashed curve (- - -). As can be seen from the figure, the diffusion coefficient varies about an order in the entire κ -range of 0.9 Å^{-1}≤ κ ≤ 4.6 Å^{-1}. The diffusion coefficient acquires the κ -dependant form in the present theory and is obtained to generate that justify the zeroth sum rule of liquid along with the other sum rules. This significant sum rule (zeroth sum rule) has not been obeyed by the dynamical generated by the microscopic theory of HB 7. In Figure 4, results for $S(\kappa, \omega)$ obtained from two theories have been obtained for smaller κ values: (——) present modified theory and (- - -) HB theory for κ =0.9 Å^{-1}, κ =1.2 Å^{-1}, κ =1.4 Å^{-1} and κ =1.8 Å^{-1}. The comparative advancement of results from present theory is clearly evident from the figure where the outcomes from older microscopic theory (HB) are much sharper as compared to the results of present theory which provides a more realistic picture.
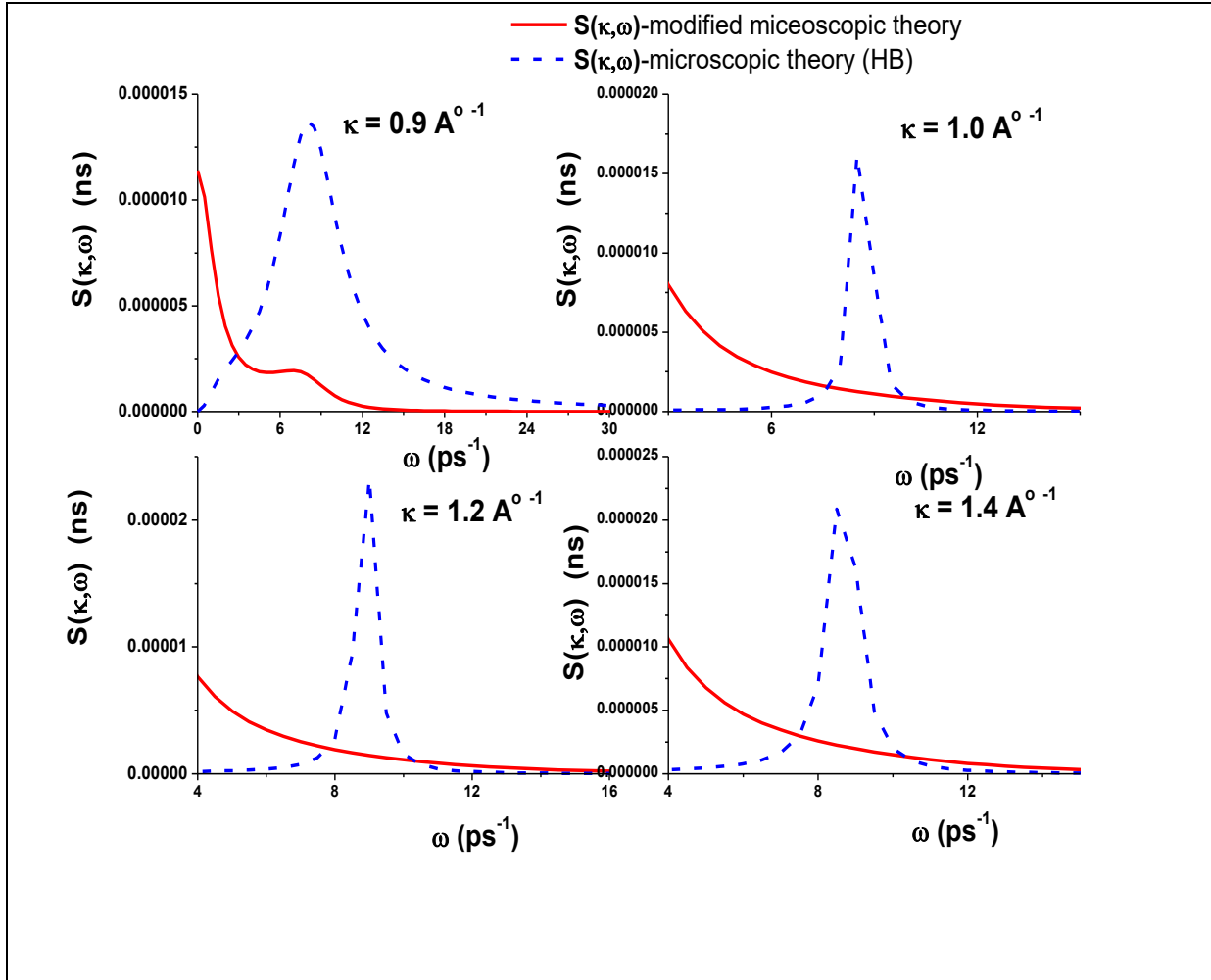
Figure 4: Variation of the dynamical structure factor, $S(\kappa, \omega)$ of liquid mercury at 523 K with frequency, ω under different considerations: (——) present theory; (- - -) older HB theory.

Figure 5(a) presented the evaluated results of $C(\kappa, \omega)$, current-2 correlation function, derived from the dynamical structure factors as two are connected through expression (6). for different wave-vector k values and has been drwan as their variation against ω: (——) $\kappa = 0.9$ Å^{-1}; (——) $\kappa = 1.2$ Å^{-1}; (——) $\kappa = 1.4$ Å^{-1}; (——) $\kappa = 1.6$ Å^{-1}; (——) $\kappa = 1.8$ Å^{-1}; (——) $\kappa = 2.0$ Å^{-1}; (——) $\kappa = 2.4$ Å^{-1}; (——) $\kappa = 2.7$ Å^{-1}; (——) $\kappa = 3.0$ Å^{-1}; (——) $\kappa = 3.5$ Å^{-1}; (——) $\kappa = 4.0$ Å^{-1}; (——) $\kappa = 4.3$ Å^{-1}; (——) $\kappa = 4.6$ Å^{-1}. The peak positions of current-2 correlation functions provide the collective mode frequencies of given liquid.
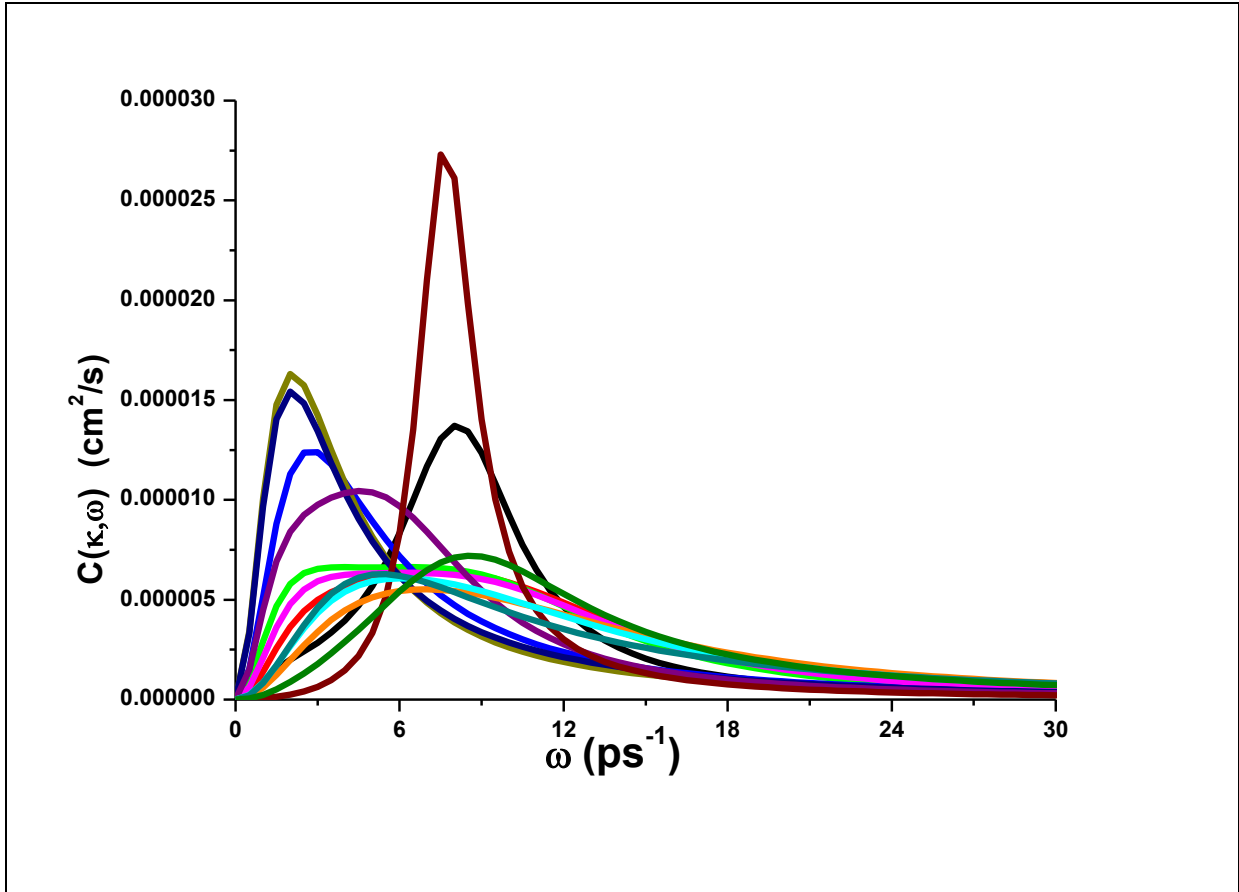
Figure 5: Current-2 correlation functions $C(\kappa, \omega)$ **for liquid Hg at 523 K versus** ω **for: (———)** $\kappa = 0.9$ Å^{-1}**; (———)** $\kappa = 1.2$ Å^{-1}**; (———)** $\kappa = 1.4$ Å^{-1}**; (———)** $\kappa = 1.6$ Å^{-1}**; (———)** $\kappa = 1.8$ Å^{-1}**; (———)** $\kappa = 2.0$ Å^{-1}**; (———)** $\kappa = 2.4$ Å^{-1}**; (———)** $\kappa = 2.7$ Å^{-1}**; (———)** $\kappa = 3.0$ Å^{-1}**; (———)** $\kappa = 3.5$ Å^{-1}**; (———)** $\kappa = 4.0$ Å^{-1}**; (———)** $\kappa = 4.3$ Å^{-1}**; (———)** $\kappa = 4.6$ Å^{-1}**.**

In figure 6(a), variation of the collective mode frequencies, ω_p with wave vector κ, the dispersion relation for liquid Hg at 523 K, has been plotted with a solid-square curve (-■-). The values of ω_p are predicted from the peak positions of current-2 correlation functions shown in the figure 5. As can be seen from the figure, collective modes frequencies, ω_p, first decreases to a minimum at $\kappa = 2.0$-2.4 Å^{-1}, increases with increase in κ to maximum and then decreases for higher wave-vectors. A second maxima at $\kappa = 3.5$ Å^{-1} has been seen in the figure. Hence, the usual trend for variation of ω_p versus κ, has been obtained for liquid Hg.
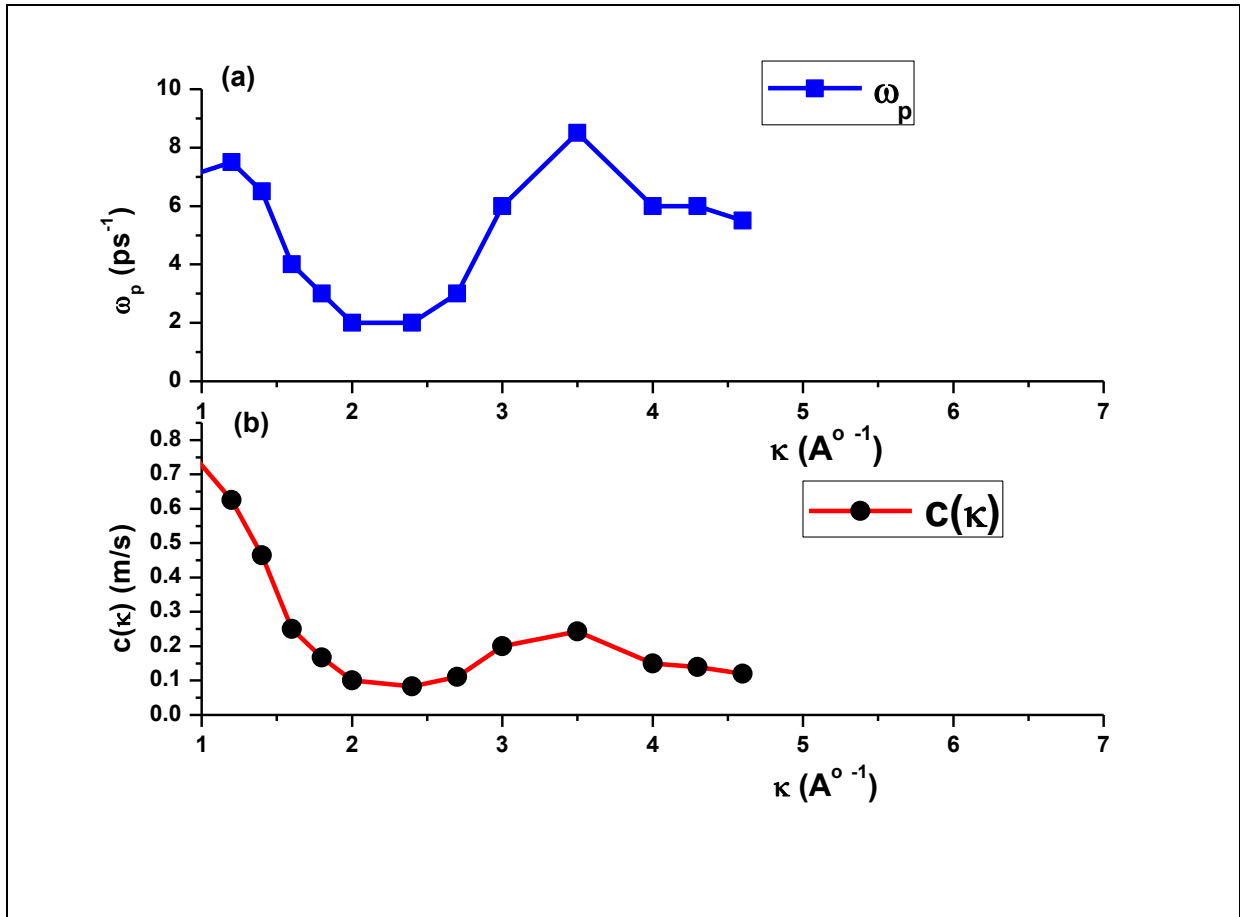
Figure 6(a): Dispersion relations for liquid Hg at 523 K from present theoretical calculations and deduced from current-2 correlation function: ω_p vs. κ : (-■-).

Figure 6(b): Velocity of sound in liquid mercury at 523 K as depicted from figure 5(a) vs. wave-vector, κ : (—■—).

Figure 6(b) shows, with a solid-circle curve (-●-) the velocities of sound as obtained from the dispersion relation ($=\omega_p/\kappa$) of figure 6(a) and have been shown as their variation against κ. The computed sound velocity are expected to agree with the experimental measurements at κ =0 and in present theory can be evaluated for $\kappa \rightarrow 0$ 17 to be 2.4 km/s.

4. CONCLUSION

The study can be concluded to effectively foretell the collective dynamics of liquid Hg at 523 K using the modified microscopic theory which is a way better than the older microscopic theory. This theoretical approach, incorporates particle correlations by defining the relaxation time to account for inter-particle interactions and It provides a means to calculate key properties such as the diffusion coefficient, collective modes, and sound

velocity. The defines relaxation time to include distinct particle correlations and yields diffusion coefficient, collective modes, and the velocity of sound

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