Research Article

Collective Dynamics of an Alkali Metal: Liquid Na

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Abstract— The detailed coherent dynamical structure factor of liquid Na at 390 K, in the wave-vector range, 1.6 Å^{-1} ≤ κ ≤ 6.5 Å^{-1}, has been predicted by the modified microscopic theory of the collective dynamics of a simple liquid. The wave-vector range corresponds to the primary peak position and the subsequent κ values of the static pair correlation function. The computed values of the dispersion relation, the velocity of sound and the diffusion coefficient have also been reported. The dynamical structure factors yielded by the modified microscopic theory satisfy the zeroth sum rule along with other sum rules of liquids.

Keywords— Dynamical structure factor,, Diffusion coefficient; Modified microscopic theory, Dispersion relation, Interaction Potential, Current-current correlation function

1. Introduction

A coherent dynamical structure factor is obtained when van-Hove space-time dependent correlation function is Fourier transformed over space-time. The van-Hove space-time dependent correlation function is the time generalized static pair correlation function. Thus, the dynamical structure factors can provide comprehensive information about the dynamical behaviour of the system. Here, a system can be an ordered system which has lattice translational invariance or can be disordered like gases. Distinguished experimental techniques like thermal neutron inelastic scattering or inelastic X-ray scattering can be used to study the coherent motion of interacting particles of a system However, these techniques have some limitations; owing to significant neutron-nucleus interaction-induced incoherent scattering, it is challenging to derive a coherent dynamical structure component from inelastic thermal neutron scattering data: the proportion. Inelastic X-ray scattering, on the other hand, can provide pure coherent structures when performed on the highly resolved synchrotron radiation sources. Unlike Rubidium and Cesium [1-4], whose INS carries predominately coherent data, scattering cross-sections of INS spectra for liquid Na carries comparable amounts of coherent and incoherent parts, the ratio is 0.99 and is not able to provide information regarding the collective dynamics of liquid metal. However, Inelastic X-ray scattering (IXS) experiments [5], which use high-flux with an energy of 21.747 keV of the incident photons, performed at high resolution third-generation synchrotron sources, can provide the pure coherent data and such an experiment has been performed to measure spectral lineshapes of essentially coherent $S(\kappa,\omega)$ of liquid Na near its melting temperature, at 390 K. The IXS experiment precisely identifies the small momentum transfer region 0.15 Å^{-1} ≤ κ ≤ 1.46 Å^{-1}, i.e., $\kappa <$ κ_m which is the wave-vector value where the first peak of the static structure factor is positioned and is the significant region for the system's collective dynamics. Hence, a comprehensive spectral lineshape of $S(\kappa,\omega)$ is obtained, which includes all pertinent details regarding the entire collective dynamics of the liquid sodium is available only for small momentum transfers. Higher wave vector region $\kappa > \kappa_m$, however, remained unreported and hence, no experimental data for collective dynamics in this region of Na is provided by the IXS experiment.

In the current study, the dynamical structure factor and hence, collective dynamics of liquid Na has been predicted using an approach that involves the microdynamics of liquid. The current theory assess the reaction of the correlated and interacting particles of the fluid to an external radiation, by solving the equations of motion for moving particles carrying time-dependant disorders and then taking appropriate history averages of their paths [6]. The Fluctuation-dissipation theorem describes the connection between the space-time-Fourier transform of the imaginary part of the response function $\chi(\kappa,\omega)$ to the dynamical structure factor $S(\kappa,\omega)$. The neglected correlations between distinct particles are assimilated into the theory by defining a distinctive characteristic relaxation time, which, further, is dependent upon the static structure factor, density, temperature, mass, interaction potential, and the diffusion coefficient. In the

theoretical approach, the diffusion coefficient is generalized to a wave-vector dependant identity that takes a specific value for a given κ. A further modification to theory has been incorporated to explain the experimentally measured $S(\kappa,\omega)$ for fluids to make a realistic depiction of $F_s(\kappa,t)$, the intermediate self-scattering function, is attained by making only the diffusion coefficient frequency ω dependent instead of a number of arbitrary parameters. With this theoretical method, collective dynamics of a number of liquids has previously been explained successfully [7-11]. In the present communication, this form of the modified microscopic theory has been implied to investigate the collective dynamics of liquid Na.

This Paper is organized in five sections. Section one lays an introductory foundation to the research field of current study. In section 2, a brief review of the previous work carried in the field is made. Section 3 draws theoretical layout and mathematical formalism used to find the outcomes of the research work and section 4 contains results and figures for the performed computations along with related discussions. Section 5 conclusions drawn from the study are narrated.

2. Related Work

As described in section 1, the dynamical structure factor is related to $\chi''(\vec{\kappa},\omega)$ which is the imaginary part of the Fourier transform of the density-2 response function, through the well-known Fluctuation-Dissipation Theorem and is given as:

$$S(\vec{\kappa},\omega)=-\frac{k_B T}{\pi\rho_0}\frac{\chi''(\vec{\kappa},\omega)}{\omega}$$

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

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

(1)

In the expression (1), $\beta'' = D_{eff}\kappa^2$, D_{eff} is ω–dependant diffusion coefficient, and $\beta=(k_B T)^{-1}$.

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

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

(2)

And, $\gamma\equiv\gamma(\kappa)=1/\tau(k)$, where is the relaxation time defined in the present theory as follows:

Here, $\chi(\vec{\kappa},\omega)$ is a complex function obtained when the density-2 response function is Fourier transformed and $\chi''(\vec{\kappa},\omega)$ is the imaginary part of the $\chi(\vec{\kappa},\omega)$.

T denotes the temperature and ρ_o is the number density of particles.

Density-2 response function accounts for the response of any liquid when perturbed with a weak external probe to generate space-time dependant fluctuations in equilibrium density. Microscopic theory describes an approach to find the $\chi(\vec{\kappa},\omega)$ function by solving micro-dynamics of the liquid. Trajectories of moving particles are depicted from the solution of classical equations of motion whose history averages provide further analysis by defining intricate space-time dependant correlation functions. In the earlier microscopic theory, the time dependant correlations were neglected and hence, the dynamical structure factors generated were far away from the experimentally observed spectral lineshapes. To include the neglected correlations, a characteristic relaxation time is introduced so as to satisfy the zeroth sum rule. The modified microscopic theory is then applied to yield much better results for dynamical structure factors for a variety of liquids [12-16].

3. Theory and Mathematical Formalism

The dynamical structure factor in the above described modified microscopic theory is expressed as:

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

(3)

In the expression (3) $\beta' = D\kappa^2$, D is the diffusion coefficient, m is the atomic mass and $S(\kappa)$ is the static structure factor given as follows:

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

(4)

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

$$\omega_E{}^2 = \frac{4\pi\rho_0}{3m}\int\left(\frac{\partial^2 V}{\partial r^2}+\frac{2}{r}\frac{\partial V}{\partial r}\right)g(r)r^2 dr \qquad (5)$$

And peak $r = r_0$ of the delta function

$$\frac{\partial^2 V}{\partial z^2}g(r) = A\delta(r-r_0) \qquad (6)$$

Here, $g(r)$ is the static pair correlation function and z is space coordinate.

$V(r)$, here, is the inter-atomic potential

The current-current correlation function $C(\kappa,\omega)$ can be expressed in terms of the dynamical structure factor as follows:

$$C(\kappa,\omega)=(\omega^2 S(\kappa,\omega))/\kappa 2 \qquad (7)$$

4. Results and Discussion

As is discussed earlier, high resolution inelastic X-ray scattering (IXS) for liquid sodium at 390 K has been reported only for low momentum transfers, $\kappa \le 1.46$ Å^{-1} and hence, theoretical computations of dynamical structure factors for a liquid of Na atoms comprising a density of 0.927 g/cc at 390 K for higher wave-vector values ($\kappa > 1.46$ Å^{-1}) are attempted in the preset study. The modified microscopic theory

described in the introduction and mathematical sections require the interaction potential to be known. Though a number of interatomic potentials for liquid Na, computed either as in an algebraic forms or deduced from any dependant quantity, have been reported in the literature, an interatomic interaction potential suggested by Paskin and Rahman [17] has been used for the present investigation. This potential form suggested by the Paskin et al. has successfully reproduced the experimental static structure factor $S(\kappa)$ [18] and hence, has been chosen here. This form of interatomic potential carries Friedel oscillations in the long-range oscillatory part, originated due to the presence of ionic charges in the liquid, along with a soft repulsive core of Born-Mayer kind. When compared to the other two succeeding alkali metals, in the periodic table, liquid cesium (Cs) and liquid rubidium (Rb) [16] near their melting points, these alkali metals though, are similar to Na in consisting of repulsive and oscillatory parts, are exhibiting larger cycles for oscillations and the nearest neighbour distances, which can be attributed to their larger atomic radius. One can see that with the parameters of this potential, value for the de-Boer parameter for Na turns out to be 0.174. Here, $\Lambda\left(=\frac{h}{\sigma\sqrt{m\varepsilon}}\right)$

ε is the depth of the inter-atomic potential and h is the Planck's constant. Λ here is much less than one. Therefore, one can treat molten Na as essentially a classical system. the experimentally measured static pair correlation function $g(r)$ [18] and the interaction potential $V(r)$ when collectively substituted in expression (5) to yield the Einstein

frequency ω_E and r_0 for liquid Na to be 1.307×10^{13} s^{-1} and 3.5 Å, respectively. While these two entities are further substituted into expression (2) to evaluate ω_κ, the static structure factor $S(\kappa)$ is evaluated by the Fourier transform of static pair correlation function $g(r)$ using expression (4). The characteristic relaxation time $\tau(\kappa)$, introduced in the present form of modified microscopic theory to incorporate distinct correlations, is evaluated by substituting calculated values of ω_κ and $S(\kappa)$ in to expression (3) and value of the diffusion coefficient, D, is adjusted to obtain the fulfilment of the zeroth sum rule for a given value of wave-vector κ. The detailed dynamical structure factors can now be calculated using expression (1).
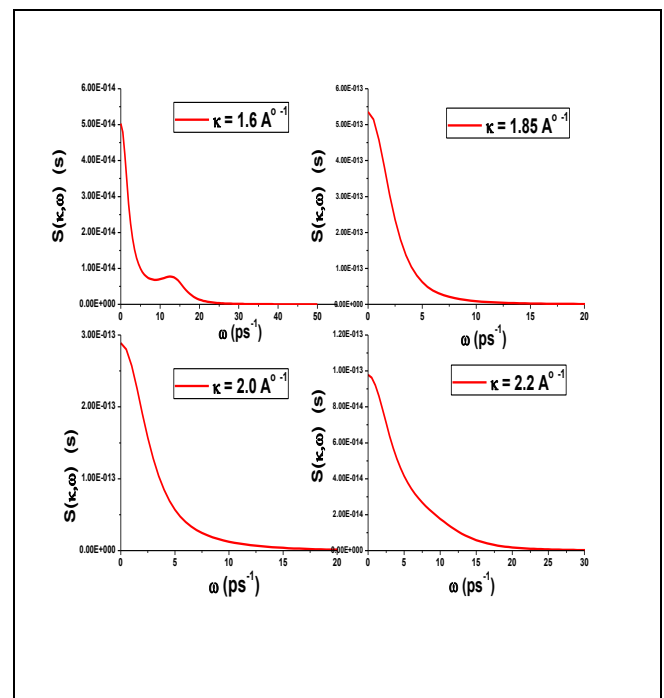
Figure 1: Variation of the dynamical structure factor, $S(\kappa,\omega)$ of liquid sodium at 390 K with frequency, ω, at : (——) at κ =1.6 Å^{-1}, κ = 1.85 Å^{-1}, κ = 2.0 Å^{-1} and κ =2.2 Å^{-1}.

The dynamical structure factors, $S(\kappa,\omega)$, using expression (1), have been calculated for thirteen wave-vector values: in a wide wave-vector range, 1.6 Å^{-1} ≤ κ ≤ 6.5 Å^{-1}. The chosen range of wave-vector corresponds to $\kappa > \kappa_m$, region of the static structure factor for which IXS values of $S(\kappa,\omega)$ have not been reported. The computed results for dynamical structure factors $S(\kappa,\omega)$, as their variation with frequency, ω, have been shown for different values of κ in Figure 1: κ =1.6 Å^{-1}; κ =1.85 Å^{-1}; κ =2.0 Å^{-1} and κ =2.2 Å^{-1} with solid curve (——). Similar variations have been shown in Figure 2: κ =2.5 Å^{-1}; κ =3.0 Å^{-1}; κ =3.5 Å^{-1} and κ =4.0 Å^{-1} with solid curve (——) and also in Figure 3: κ =4.5 Å^{-1}; κ =5.0 Å^{-1}; κ =5.5 Å^{-1} and κ =6.0 Å^{-1} and κ =6.5 Å^{-1} with solid curve (——). In these computations, D$_{eff}$ is taken to be equal to the diffusion

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coefficient occurring in expression (3). This can be evidently seen from the figures 1, 2, 3 that for higher wave
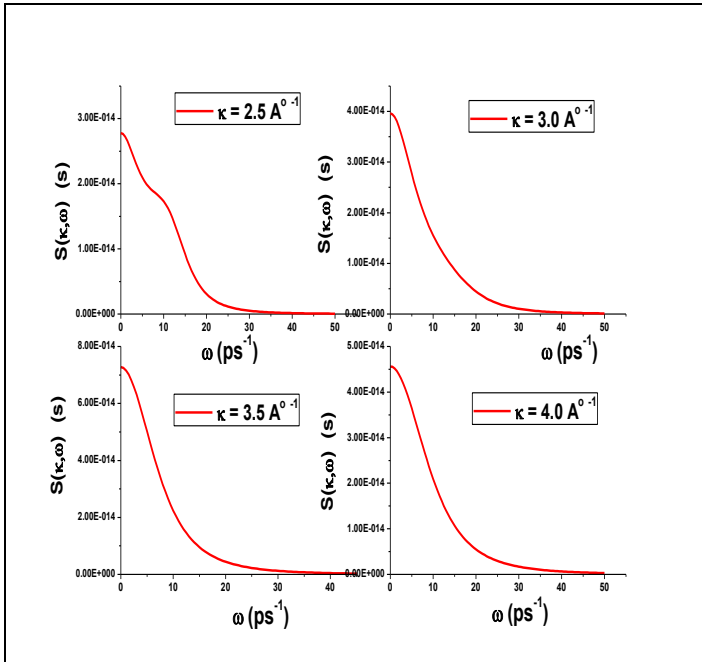

Figure 2: Variation of the dynamical structure factor, $S(\kappa, \omega)$ of liquid sodium at 390 K with frequency, ω, at : (——) at κ = 2.5 Å^{-1}, κ = 3.0 Å^{-1}, κ = 3.5 Å^{-1} and κ =4.0 Å^{-1}.

vectors the dynamical structure factors are damped in appearance with no Brillouin peaks are observed, except for κ =1.6 Å^{-1}. This is in contrast to S(κ, ω) calculated (and also measured experimentally through IXS) for smaller wave vector values, κ <1.6 Å^{-1}, reported previously [16], where clear shoulder peaks at $\omega = \omega_p$ have been observed.
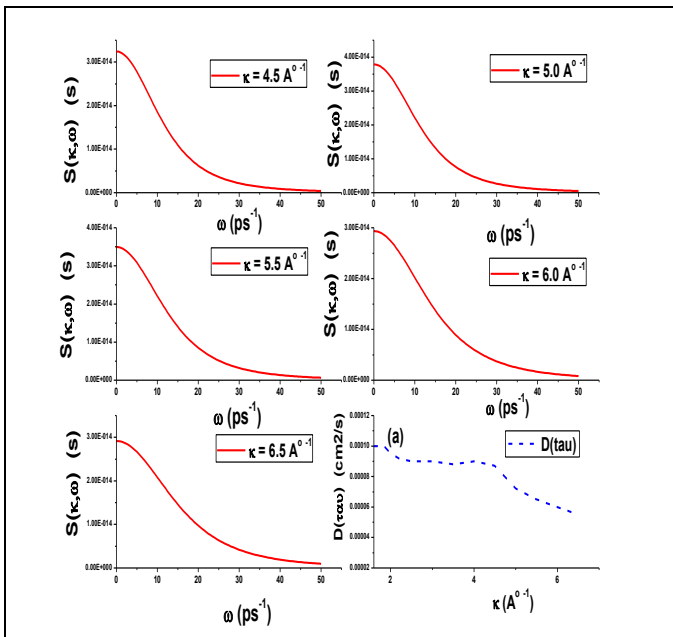

Figure 3(a): Variation of Diffussion Co-efficient with wave-vector κ as discussed in text.

The self-Diffusion coefficient turns out to be a parameter in the theory to fulfil the zeroth sum rule and hence, acquires the κ-dependant form in the present theory. The obtained values of the diffusion coefficient have been shown in Figure 3(a) as against wave-vector k : with dashed curve (- - -). In the entire κ-range of 1.6 Å$^{-1} \leq \kappa \leq$ 6.5 Å^{-1}, the overall variation of D is merely half an order and this can further be observed when including the previous study [16] in the smaller κ region 0.3 Å$^{-1} \leq \kappa \leq$ 1.46 Å^{-1} that the total variation of self-diffusion remains lesser than two orders. In Figure 4, computed results of $C(\kappa, \omega)$, the current-2 correlation function deduced from the computed dynamical structure factors, using expression (6) for different values wave-vector k has been shown as their variation against ω: (——) κ = 1.6 Å^{-1}; (——) κ =1.85 Å^{-1}; (——) κ = 2.0 Å^{-1}; (——) κ = 2.2 Å^{-1}; (——) κ = 2.5 Å^{-1}; (——) κ = 3.0 Å^{-1}; (——) κ = 3.5 Å^{-1}; (——) κ = 4.0 Å^{-1}; (——) κ = 4.5 Å^{-1}; (——) κ = 5.0 Å^{-1}; (——) κ = 5.5 Å^{-1}; (——) κ = 6.0 Å^{-1}; (——) κ = 6.5 Å^{-1}. Current-2 correlation functions are single-peak structures unlike dynamical structure factors that can exhibit two peaks, one at zero frequency position and another is shoulder peak at collective mode frequency position. The peak positions of current-2 correlation functions provide the collective mode frequencies of given liquid.
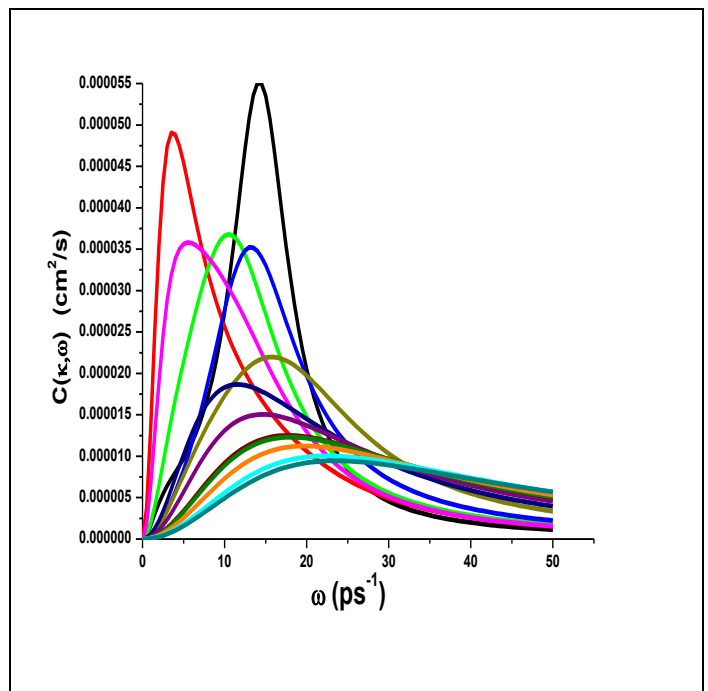
Figure 4: Current-2 correlation functions for liquid Na at 390 K versus ω for: (——) κ = 1.6 Å^{-1}; (——) κ = 1.85 Å^{-1}; (——) κ = 2.0 Å^{-1}; (——) κ = 2.2 Å^{-1}; (——) κ = 2.5 Å^{-1}; (——) κ = 3.0 Å^{-1}; (——) κ = 3.5 Å^{-1}; (——) κ = 4.0 Å^{-1}; (——) κ = 4.5 Å^{-1}; (——) κ = 5.0 Å^{-1}; (——) κ = 5.5 Å^{-1}; (——) κ = 6.0 Å^{-1}; (——) κ = 6.5 Å^{-1}.

In figure 5(a), the dispersion relation for liquid Na at 390 K has been shown with a solid-square curve (-■-). The values of ω_p are the peak positions of computed current-2 correlation functions for different wave-vector values when plotted against the frequency ω. As can be observed from the figure, the frequencies of collective modes, ω, first decreases to a minimum at $\kappa = 1.85$ Å^{-1}, wave-vector corresponding to peak position of static structure factor to complete the first Brillouin zone and then keep increasing for higher wave-vector. A mild second minima at $\kappa = 3.5$ Å^{-1} has also been seen in the figure. Hence, the usual form of dispersion relation has been obtained for liquid Na in the entire wave-vector range. Figure 5(b) displays with a solid-circle curve the velocities of sound as deduced from the dispersion relation of figure 5(a) and have been plotted
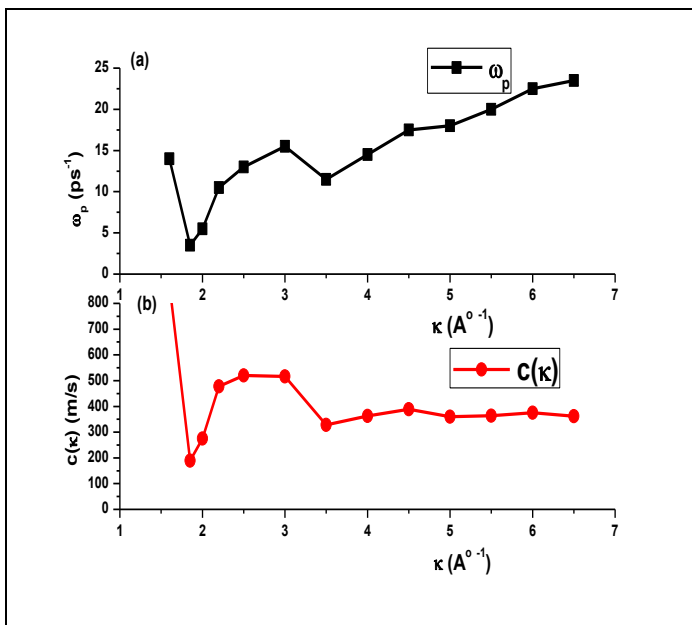
Figure 5(a): Dispersion relations for liquid Na at 390 K from present theoretical calculations and deduced from current-2 correlation function: ω_p vs. κ : (-■-).

Figure 5(b): Velocity of sound in liquid sodium at 390 K as depicted from figure 5(a) vs. wave-vector, κ : (—■—).

as their variation against κ. One can compute the sound velocity from the linear region of the dispersion relation, obtained for smaller κ values [16], the region not considered here.

5. Conclusion and Future Scope

This may be concluded from the study that the collective dynamics of liquid Na at 390 K can be predicted through a theoretical approach that involves the solution of equations of motion of moving particles of the system. This approach, modified microscopic theory, defines relaxation time to include distinct particle correlations and yields diffusion coefficient, collective modes, and the velocity of sound. Collective dynamics of a variety of liquid with different physical conditions can, therefore, be predicted with this theoretical approach for various applications.

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