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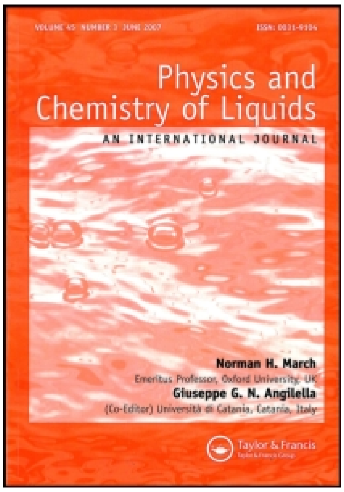

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Collective Density Excitations in Liquid Cesium

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COLLECTIVE DENSITY EXCITATIONS IN LIQUID CESIUM

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Using the Mori-Zwanzig memory function formalism with an hyperbolic secant form for the second order memory function, we calculate the dynamical structure factor of liquid Cesium at its melting point. The two parameters appearing in the memory function are determined from the sum rules of the density-density correlation function. The required inputs are an interatomic potential and the corresponding pair correlation function. The calculations are performed with the Price-Singwi-Tosi potential for liquid metals and the predicted results for $S(q,\omega)$ show collective density excitations for wave numbers $q \leqslant 1$ Å^{-1}, in agreement with experimental results.

KEY WORDS: Collective density excitations, dynamical structure factor, memory function, liquid cesium.

1. INTRODUCTION

Collective density excitations are characterized by the appearance of a distinct peak, at a finite frequency ω, in the dynamical structure factor $S(q,\omega)$ for small wave vectors q. Recently, inelastic neutron scattering experiments on liquid Cesium at its melting point have been performed[1,2] and these show the existence of a well-defined collective peak for $q \leqslant 1$ Å^{-1} which disappears for $q > 1.2$ Å^{-1}. These results are not very different from those for other liquid metals[3,4,5]. In order to better understand the behaviour of liquid alkali metals, we, in the present work, apply a theoretical procedure developed earlier[6,7] to calculate the dynamic structure factor for liquid Cesium. The procedure is based on the Mori-Zwanzig memory function formalism[8] and on the use of a secant hyperbolic form for the second-order memory function. The two parameters appearing in the phenomenological memory function are determined from the frequency sum rules of the density-density correlation function. This approach has been quite successful in reproducing the essential features of $S(q,\omega)$ in both liquid Argon[6] and liquid Aluminium[7].

The only inputs in our theory are the second- and fourth-frequency moment sum rules of the longitudinal current-current correlation function. Expressions for these moments are known[6] and they involve the interaction potential and the static pair and triplet- correlation functions. To study liquid Cesium we use the Price-Singwi-Tosi (PST) pseudo-potential[9] and the pair distribution function $g(r)$ generated by molecular dynamics[10]. The Kirkwood superposition approximation is used to approximate the triplet correlation function. It has been demonstrated by Balacuni *et al*[10] and by Ranganathan *et al*[11] that the predicted results of the PST potential for the static structure factor $S(q)$, the diffusion coefficient and the peak position of the longitudinal current correlation function are in very good agreement with experimental results. Our results of $S(q,\omega)$, when compared with experimental data, indicate that our model is capable of predicting the correct collective density excitations in liquid Cesium. However, our model does not reproduce the correct small frequency behaviour for small wave vectors.

In section 2, we present the features of our theoretical model. The results and discussions are presented in section 3. Section 4 contains the summary and conclusions.

2. MODEL

In the Mori-Zwanzig projector operator formalism, the density-density correlation function satisfies an integro-differential equation

$$\frac{\partial F(q,t)}{\partial t} = -\int_0^t F(q,\tau) M_1(q,t-\tau)\, d\tau \tag{1}$$

where $M_1(q,t)$ is the first-order relaxation kernel or memory function. Defining the Fourier-Laplace transform as

$$\tilde{F}(q,\omega) = i\int_0^\infty F(q,t) e^{i\omega t} dt \tag{2}$$

we obtain from (1)

$$\tilde{F}(q,\omega) = -\frac{\beta F(q,t=0)}{\omega + \tilde{M}_1(q,\omega)} \tag{3}$$

where $F(q,t=0) = S(q)$, the static structure factor, and $\beta = (k_B T)^{-1}$, with T as the temperature. The dynamic structure factor $S(q,\omega)$ is given by

$$S(q,\omega) = 2k_B T \tilde{F}''(q,\omega) \tag{4}$$

where $\tilde{F}''(q,\omega)$ is the imaginary part of $\tilde{F}(q,\omega)$. It also follows from the projector operator formalism that $M_1(q,t)$ satisfies an equation similar to (1), the Fourier-Laplace transform of which is given by

$$\tilde{M}_1(q,\omega) = -\frac{M_1(q,t=0)}{\omega + \tilde{M}_2(q,\omega)} \tag{5}$$

where $\tilde{M}_2(q,\omega)$ is the second-order memory function. From (3) and (5), we obtain

$$\tilde{F}(q,\omega) = \frac{-\beta S(q)\,[\omega + \tilde{M}_2(q,\omega)]}{\omega^2 + \omega \tilde{M}_2(q,\omega) - \delta_1} \tag{6}$$

where $\delta_1 = M_1(q,t=0) = q^2 k_B T/mS(q)$. We finally obtain from (4) and (6), the expression for $S(q,\omega)$, given by

$$S(q,\omega) = \frac{2q^2 k_B T \tilde{M}''_2(q,\omega)/m}{[\omega^2 - \delta_1 + \omega \tilde{M}'_2(q,\omega)]^2 + [\omega \tilde{M}''_2(q,\omega)]^2} \tag{7}$$

In our earlier work[6,7], we used a hyperbolic secant form for the relaxation kernel to study the dynamics of liquid Aluminium and dense Argon fluid. It was found that this procedure gave a reasonable description of the main dynamical features, as expressed by the dynamic structure factor. We wish to apply the same phenomenological form of the memory function to study the dynamics of a liquid metal in the alkali series, liquid Cesium, for which recent experimental data on the dynamic structure factor have been published[2]. Thus we approximate the second-order memory function by

$$M_2(q,t) = a\,sech(bt) \tag{8}$$

It is to be noted that this form of the memory function has a Gaussian behaviour for short times and an exponential behaviour at large times and in this sense is a reasonable and an appropriate expression to use in a study of the dynamics of a fluid for all times.

In order to understand the origin of equation (8), we write Mori's equation for second- and third- order relaxation kernel in Fourier-Laplace space. These are given by

$$\tilde{M}_2(q,\omega) = -\frac{M_2(q,t=0)}{\omega + \tilde{M}_3(q,\omega)} \tag{9}$$

$$\tilde{M}_3(q,\omega) = -\frac{M_3(q,t=0)}{\omega + \tilde{M}_4(q,\omega)} \tag{10}$$

Eliminating $\tilde{M}_3(q,\omega)$ and taking the inverse transform of the resulting equation, we obtain

$$\frac{\partial^2 M_2(q,t)}{\partial t^2} + b^2 M_2(q,t) + \int_0^t M_4(q,t-\tau)\frac{\partial M_2(q,\tau)}{d\tau}d\tau = 0 \tag{11}$$

where $b^2 = M_3(q, t=0)$. It can be shown[12] that under certain conditions, the above equation reduces to

$$\frac{\partial^2 M_2(q,t)}{\partial t^2} - b^2 M_2(q,t) + \frac{2b^2}{a^2} M_2^3(q,t) = 0 \tag{12}$$

with $a = M_2(q, t=0)$, which is a well-known equation in nonlinear dynamics and whose solution is known to be a secant hyperbolic function, given by equation (8).

The real and imaginary parts of $\tilde{M}_2(q,\omega)$ are given by[13]

$$\tilde{M}'_2(q,\omega) = \frac{\pi a}{2b}\tan h\left(\frac{\pi\omega}{2b}\right) + \frac{ia}{2b}\left[\Psi\left(\frac{b+i\omega}{4b}\right) - \Psi\left(\frac{b-i\omega}{4b}\right)\right] \tag{14}$$

and

$$\tilde{M}''_2(q,\omega) = \frac{\pi a}{2b} sech\left(\frac{\pi\omega}{2b}\right) \tag{15}$$

where $\Psi(x)$ is the Euler Psi function. The two parameters **a** and **b** appearing in the memory function are determined by incorporating exactly the short time behaviour. We thus obtain

$$\mathbf{a} = \boldsymbol{\delta}_2 = \omega_l^2(q) - \boldsymbol{\delta}_1$$

and

$$\mathbf{b}^2 = \boldsymbol{\delta}_3 = \frac{[\boldsymbol{\Omega}_l^4(q) - (\omega_l^2(q))^2]}{\delta_2}. \tag{16}$$

In the above equations, $\omega_l^2(q)$ and $\Omega_l^4(q)$ are the second and fourth frequency moment sum rules of the longitudinal current-current correlation function. Expressions for these quantities have been given in our earlier work[6].

3. RESULTS AND DISCUSSION

In order to calculate $S(q,\omega)$ from (7), we require $\omega_l^2(q)$ and $\boldsymbol{\Omega}_l^4(q)$. These depend on the interatomic potential $u(r)$ and its first-, second-, and third-order derivatives, the pair distribution function $g(r)$ and the triplet correlation function. For the potential, we have chosen the Price-Singwi-Tosi potential[9] which is known to describe the alkali series liquid metals reasonably well. The well-depth ϵ of the potential is 385.5 K and the position $\boldsymbol{\sigma}$ of the first zero of the potential is 4.761 Å, corresponding to Cesium at its melting point (temperature $T = 302$ K and number density $n = 0.0083$ Å^{-3}). The derivatives of the potential were obtained using a five-point differential formula. The pair distribution function $g(r)$ was obtained in our earlier work[11] which was found to be in very good agreement with experimental results. For the triplet correlation function, which appears only in the expression for $\Omega_l^4(q)$, we have used the Kirkwood superposition approximation. Previous studies[14,15] indicate that the errors introduced, in the calculation of the sum rules using this approximation, are minimal. The numerical integration was performed using Gauss quadrature. Results for $\omega_l^2(q)$ and $\Omega_l^4(q)$ are plotted in Figures 1 and 2 as a function

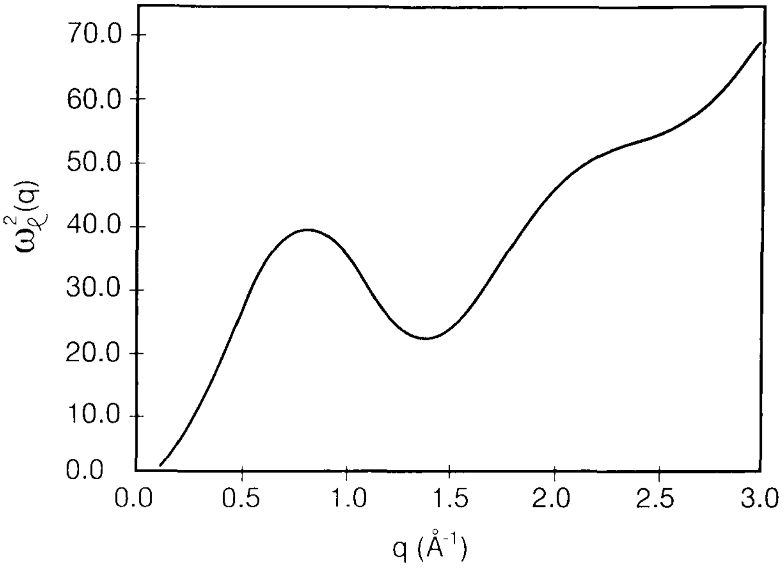

Figure 1 Variation of $\omega_l^2(q)$ of liquid Cesium at its melting point, with wave number q.

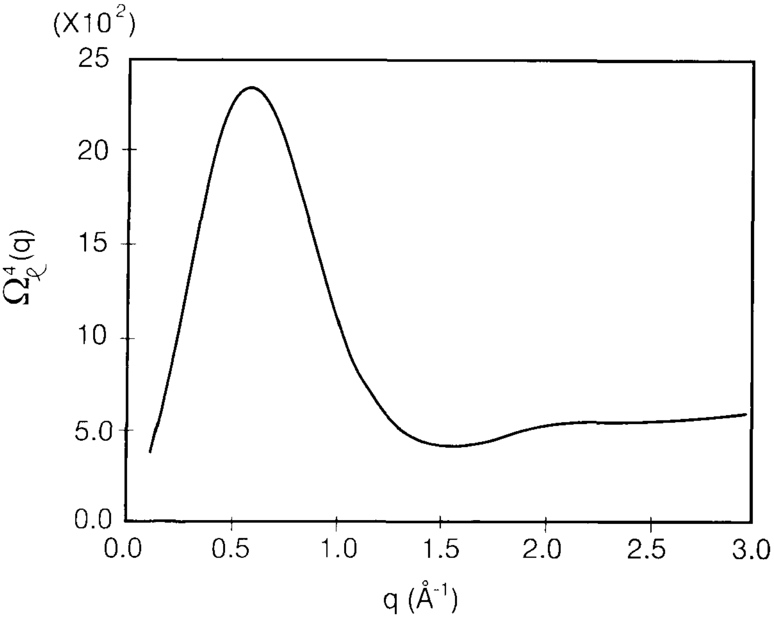

Figure 2 Variation of $\Omega_l^4(q)$ of liquid Cesium at its melting point, with wave number q.

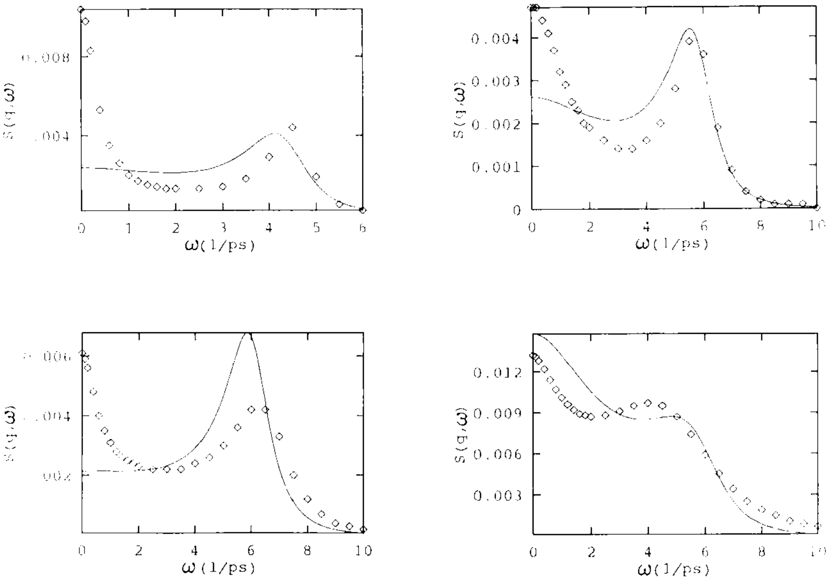

Figure 3 Plots of the dynamic structure factor $S(q,\omega)$ of liquid Cesium at its melting point as a function of ω for $q =$ a) 0.4, b) 0.6, c) 0.8 and d) $1.0\,\text{Å}^{-1}$. Our results are shown as lines and experimental results as diamond symbols.

of the wave vector q. The parameters a and b are then obtained from (16), which, when substituted in (14) and (15), yield the real and imaginary parts of the memory function $\tilde{M}_2(q,\omega)$. The dynamical structure factor $S(q,\omega)$ is then calculated from (7). These results are shown in Figures 3 and 4 as a function of the frequency ω, for various values of the wave number q. The q values in Fig. 3 are a) 0.4, b) 0.6, c) 0.8, and d) $1.0\,\text{Å}^{-1}$. Our results are shown as lines and the experimental results are shown as diamond symbols. It is seen that there is a qualitative agreement except that our theory does not reproduce the peak at $\omega = 0$. But our model does reproduce the position of the collective density excitation peak quite accurately for all the three lower values of q and the shoulder at $q = 1.0\,\text{Å}^{-1}$. The q values in Fig. 4 are a) 1.4, b) 1.6, c) 1.8, and d) $2.0\,\text{Å}^{-1}$. In this region the agreement is quite good for all values of ω. The collective peak no longer exists and out theory is able to reproduce this feature.

Thus except for the behaviour near $\omega = 0$, for low values of q, our simple theory is able to account for the experimentally observed dynamic structure factor in liquid Cesium. It is to be expected that one needs at least a two-relaxation time model to reproduce the qualitative features of the dynamic structure factor at small values of q.

4. SUMMARY AND CONCLUSIONS

In this paper we have used a hyperbolic secant form for the second-order memory function to calculate the dynamic structure factor of liquid Cesium. The two

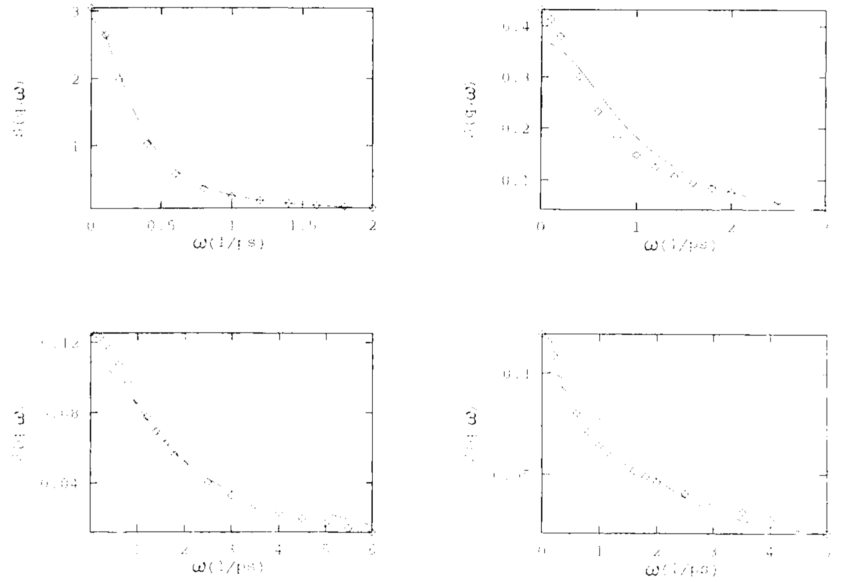

Figure 4 Plots of the dynamic structure factor $S(q,\omega)$ of liquid Cesium at its melting point as a function of ω for $q =$ a) 1.4, b) 1.6, c) 1.8 and d) 2.0 Å^{-1}. Our results are shown as lines and experimental results as mond symbols.

parameters in the memory function are determined from the frequency sum rules of the longitudinal current-current (or equivalently the density-density) correlation function. Our model predicts collective density excitations in liquid Cesium for q values less than or equal to 1.0 Å^{-1}, in complete agreement with the experimental data. The shortcoming of the model lies in the fact that the $\omega = 0$ peak is not reproduced correctly for small values of q. In order to get a better fit with experimental data, a two relaxation time model is needed as was demonstrated in a similar study of liquid Rubidium[16]. However, it is gratifying to note that a single time relaxation model is able to reproduce the collective excitations in liquid Cesium.

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