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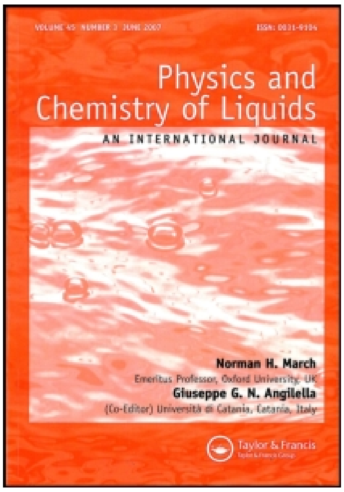

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Dynamical Structure Factor of Fluid Ar^{36}

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DYNAMICAL STRUCTURE FACTOR OF FLUID Ar^{36}

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The continued fraction representation of the correlation function and a secant hyperbolic form of the memory function have been used to calculate the dynamical structure factor $S(q, \omega)$ of fluid Ar^{36} for the densities ranging from $n^* = 0.668$ to 0.763 and a temperature to 120 K. The parameters of the memory function have been determined from the fourth and sixth frequency sum rules of $S(q, \omega)$. The predicted results for $S(q, \omega)$ have been compared with recent neutron scattering data. A good agreement has been achieved. Further, it is also found that the position of first minima of full width at half maxima of $S(q, \omega)$ shifts towards smaller wave number side with decrease in density while, the position of first maxima is independent of density.

KEY WORDS: Dynamical structure factor, memory function, fluid Argon, Sum rules.

1 INTRODUCTION

Recently the dynamical structure factor of fluid argon has been measured[1] by neutron scattering experiment for density ranging from n^* $(= n\sigma^3) = 0.668$ to 0.763 for isotherm T^* $(= k_B T/\varepsilon) = 0.974$. This provides information about the density dependence of the dynamical structure factor, $S(q, \omega)$. Physically it demonstrates the importance of the correlated collisions on the dynamical structure factor of dense fluids.

We have recently developed a phenomenological theory[2] which predicts the time evolution of the correlation functions and transport coefficients. This theory has provided very satisfactory results for the transport coefficients of Lennard–Jones (LJ) fluids over wide ranges of densities and temperatures. The assumption of the theory is a phenomenological secant hyperbolic form of the memory function whose parameters are determined from the sum rules of the appropriate correlation functions. We have also used[3] this theory to predict the dynamical structure factor of liquid aluminium. The predicted results had been found to be in good agreement with molecular dynamics data.

In this paper we analyse the neutron scattering data[1] for fluid Ar^{36} using our theory with the aim of checking the applicability of the model memory function for LJ fluids. The inputs of the theory are fourth and sixth frequency sum rules which have been calculated for LJ potential corresponding to fluid Ar^{36} using the static pair correlation function, $g(r)$ obtained from the theory of Sung and Chandler[4] and the superposition approximation for the static triplet correlation function. The results obtained for $S(q, \omega)$ have been compared with neutron scattering data at two densities along $T^* = 0.974$ isotherm. The results are found to be in good agreement for wave number $q \leq 2.5$ Å^{-1}.

In Section 2, we present the theoretical procedure for the calculation of $S(q, \omega)$. Results and discussion are given in Section 3. In Section 4, we present our conclusion.

2 THEORETICAL PROCEDURE

The Fourier–Laplace transform of the density-density correlation function in Mori–Zwanzig formalism[5] can be written as

$$\phi(q, \omega) = -\frac{\beta S(q)}{\omega + \tilde{M}_1(q, \omega)} \tag{1}$$

where $S(q)$ is the static structure factor and $\beta = (k_B T)^{-1}$. $\tilde{M}_1(q, \omega)$ is the Fourier–Laplace transform of the first order relaxation kernel or memory function (MF), $M_1(q, t)$. The dynamical structure factor is given by

$$S(q, \omega) = (2/\beta)\phi''(q, \omega) \tag{2}$$

where $\phi''(q, \omega)$ is the imaginary part of $\phi(q, \omega)$. Form Eq. (1) and (2) we find that

$$S(q, \omega) = \frac{2S(q)\tilde{M}''_1(q, \omega)}{(\omega + \tilde{M}'_1(q, \omega))^2 + (\tilde{M}''_1(q, \omega))^2} \tag{3}$$

where $\tilde{M}'_1(q, \omega)$ and $\tilde{M}''_1(q, \omega)$ are the real and imaginary parts of the $M_1(q, \omega)$. It follows from the projection operator technique used in deriving Eq. (1) that $M_1(q,\omega)$ and higher order relaxation kernal follows the equation similar to Eq. (1), given by

$$\tilde{M}_n(q, \omega) = -\frac{\delta_n}{\omega + \tilde{M}_{n+1}(q, \omega)}; \qquad n = 1, 2, 3, \ldots, \tag{4}$$

where $\tilde{M}_n(q, \omega)$ is the Fourier–Laplace transform of the nth order relaxation kernel $M_n(q, t)$, $\delta_n = M_n(q, t = 0)$ and these are related[6] to the frequency sum rules of the dynamical structure factor. Equation (4) provides a continued fraction representation for the $M_1(q, \omega)$. In order to calculate $\tilde{M}_1(q, \omega)$ from Eq. (4) it is necessary to truncate the hierarchy of Eq. (4) at some suitable stage. Higher order $\tilde{M}(q, \omega)$ are more complicated objects mathematically due to restricted time evolution of fluctuating forces. Therefore, one normally restricts the discussion to first or second order. We truncate the hierarchy of Eq. (4) at first order and obtain

$$\tilde{M}_1(q,\omega) = \tilde{M}'_1(q,\omega) + i\tilde{M}''_1(q,\omega) = -\frac{\delta_1}{\omega + \tilde{M}_2(q,\omega)} \tag{5}$$

with

$$\tilde{M}'_1(q,\omega) = \frac{-(\omega + M'_2(q,\omega))\delta_1}{(\omega + \tilde{M}'_2(q,\omega))^2 + (\tilde{M}''_2(q,\omega))^2} \tag{6}$$

and

$$\tilde{M}''_1(q,\omega) = -\frac{\delta_1 \tilde{M}''_2(q,\omega)}{(\omega + \tilde{M}'_2(q,\omega))^2 + (\tilde{M}''_2(q,\omega))^2} \tag{7}$$

where $\tilde{M}'_2$ and $\tilde{M}''_2$ are real and imaginary parts of $\tilde{M}_2(q,\omega)$. The relaxation kernel $M_2(q,t)$ is not known a priori. The relaxation kernel can be obtained microscopically using the mode–mode coupling scheme[7]. However, it is not yet clear how to extend the theory for various thermodynamic states other than those investigated near the triple point density. From the practical point of view the phenomenological forms of the relaxation kernels have played an important role in interpreting the neutron scattering data for the correlation function. In the past various phenomenolgical forms of the relaxation function have been used and results obtained have been extensively reviewed by Boon and Yip[8]. In the present paper we use our recently proposed model for the memory function namely

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

It is noted that $M_2(q,t)$ is a solution of non-linear differential equation,

$$\frac{d^2M_2(q,t)}{dt^2} - b^2M_2(q,t) + \frac{2b^2}{a^2}M_2^3(q,t) = 0. \tag{9}$$

The compatability of our predicted results with MD data/neutron scattering experiments would demonstrate the effect of non-linearity of atomic motions in fluids. It can also be noted that the memory function given by Eq. (8) tends to a Gaussian and a simple exponential for the short and long times, respectively.

The parameters 'a' and 'b' in Eq. (8) are determined from the short time properties of the memory function which are exactly known. For the present case we have

$$a = \delta_2 = \omega_l^2(q) - \delta_1; \qquad \delta_1 = q^2k_BT/mS(q) \tag{10}$$

$$b^2 = \delta_3 = (\Omega_l^4(q) - \omega_l^4(q))/\delta_2 \tag{11}$$

In Eqs (10) and (11) $\omega_l^2(q)$ and $\Omega_l^4(q)$ are second and fourth frequency sum rules of longitudinal current-current correlation function. Defining

$$\tilde{M}_2(q,\omega) = \tilde{M}'_2(q,\omega) + i\tilde{M}''_2(q,\omega) = i\int_0^\infty e^{i\omega t}M_2(q,t), \tag{12}$$

with

$$\tilde{M}'_2(q,\omega) = \frac{\pi a}{2b}\tanh\left(\frac{\pi\omega}{2b}\right) + \frac{ia}{2b}\left[\psi\left(\frac{b+i\omega}{4b}\right) - \psi\left(\frac{b-i\omega}{4b}\right)\right], \tag{13a}$$

$$\tilde{M}''_2(q,\omega) = \frac{\pi a}{2b}\operatorname{sech}\left(\frac{\pi\omega}{2b}\right) \tag{13b}$$

where $\psi(x)$ is Euler 'Psi' function defined as $\psi(x) = d/dx(\ln \Gamma(x)$ and $\Gamma(x)$ is gamma function. The dynamical structure factor $S(q, \omega)$ can be calculated using Eqs. (13), (6), (7) and (3).

3 RESULTS AND DISCUSSION

In order to calculate $S(q, \omega)$, we require the inputs δ_2 and δ_3. The calculation of δ_2 involves only the pair correlation $g(r)$ and the first two derivatives of the interatomic potential, whereas δ_3 involves upto third order derivatives of potential, $g(r)$ and static triplet correlation function $g_3(r, r')$. Although the simplified expressions for δ_2 and δ_3 has been published by Bansal and Pathak[9] but it is felt that some intermediate steps in the derivation of $\Omega_l^4(q)$ is desirable. Therefore, we present in an appendix a few intermediate steps involved in the angular integration of triplet contribution to $\Omega_l^4(q)$. The $\omega_l^2(q)$ and $\Omega_l^4(q)$ are calculated using the Lennard–Jones potential for fluid Argon and $g(r)$ obtained from the optimised cluster theory of Sung and Chandler[4]. It may be mentioned that this $g(r)$ has been found[10] to be in good agreement with MD data. For the triplet correlation function, we use the superposition approximation. The numerical results for the frequency sum rules are obtained using Gauss-quadrature method of integration. The numerical values thus obtained for frequency sum rules and experimental $S(q)$ are used to calculate δ_2 and δ_3 from Eqs (10) and (11). These are plotted in Figure 1 for Ar^{36} fluid at $T^* = 0.974$ (120 K) and $n^* = 0.668$ and 0.763 for wave numbers $q < 6.0$ Å^{-1}.

Using the above inputs, we have calculated $S(q, \omega)$ for fluid Ar^{36} at densities $n^* = 0.668$ and 0.763 for different wave numbers. These are plotted in Figures (2) and (3) respectively. Theoretical $S(q, \omega)$ shown by full line are compared with neutron scattering data represented by solid circles. From Figures (2) and (3) it can easily be seen that very good agreement has been achieved between our results and experimental data for wave number $q \leq 2.5$ Å^{-1}. The full width at half maxima (FWHM) and $S(q, \omega = 0)$ are plotted in Figures (4a) and (4b), respectively for both the densities. Here dots and crosses are the available experimental results for $n^* = 0.668$ and 0.763, respectively. It is found that the positions of maxima and minima of FWHM are predicted well and results are in good agreement for 0.8 Å^{-1} $< q \leq 2.5$ Å^{-1}. From Figure (4a) we note that the position of first maxima of FWHM (around where static structure factor shows first maxima) remain same, when the density is changed from 0.668 to 0.763. But the position of first minima shifts toward larger wave number with increase in density. Figure (4b) shows an overall good agreement for $S(q, 0)$ with experimental data for all the wavenumber. From Figure (4b) it can be seen that the

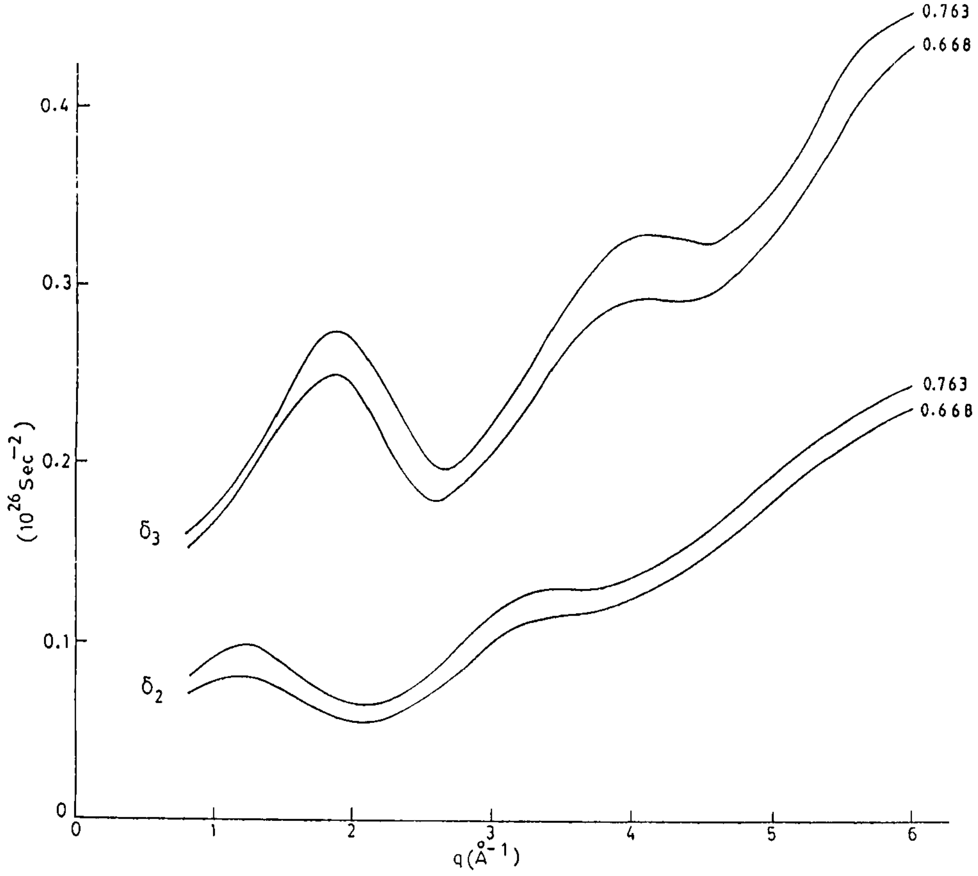

Figure 1 Variation of δ_2 and δ_3 (parameters of the memory function) with wave number q at $T^* = 0.974$ for density, (i) $n^* = 0.668$ (ii) 0.763.

position of maxima in $S(q, 0)$ shifts towards smaller wave number side as the density decreases.

In order to see the difference in dynamical structure factor of liquid aluminium calculated in our earlier work and Lennard-Jones fluids, we have plotted the second stage memory function $M'_2(q, \omega)$ and $M''_2(q, \omega)$ in Figure (5) for some values of q. From Figure (5) it can be seen that $M'_2(q, \omega)$ and $M''_2(q, \omega)$ are decreasing function of ω. On the other hand, from our earlier work on liquid Al we found that for small q, $M'_2(q, \omega)$ start from zero and decreases to attain its lowest value, then increases. As q increases the minimum flattens and finally disappears for large q. For large wave numbers both M'_2 and M''_2 were decreasing function of ω as found in present case. The difference in behaviour of $M''_2(q, \omega)$ and hence of $M_1(q, \omega)$ is responsible for the appearance and collective excitation peaks in the dynamical structure factor of liquid aluminium. In an alternative way the different behaviour of $S(q, \omega)$ for liquid Al and ^{36}Ar can be understood by examining the behaviour of $M''_1(q, \omega)$ which

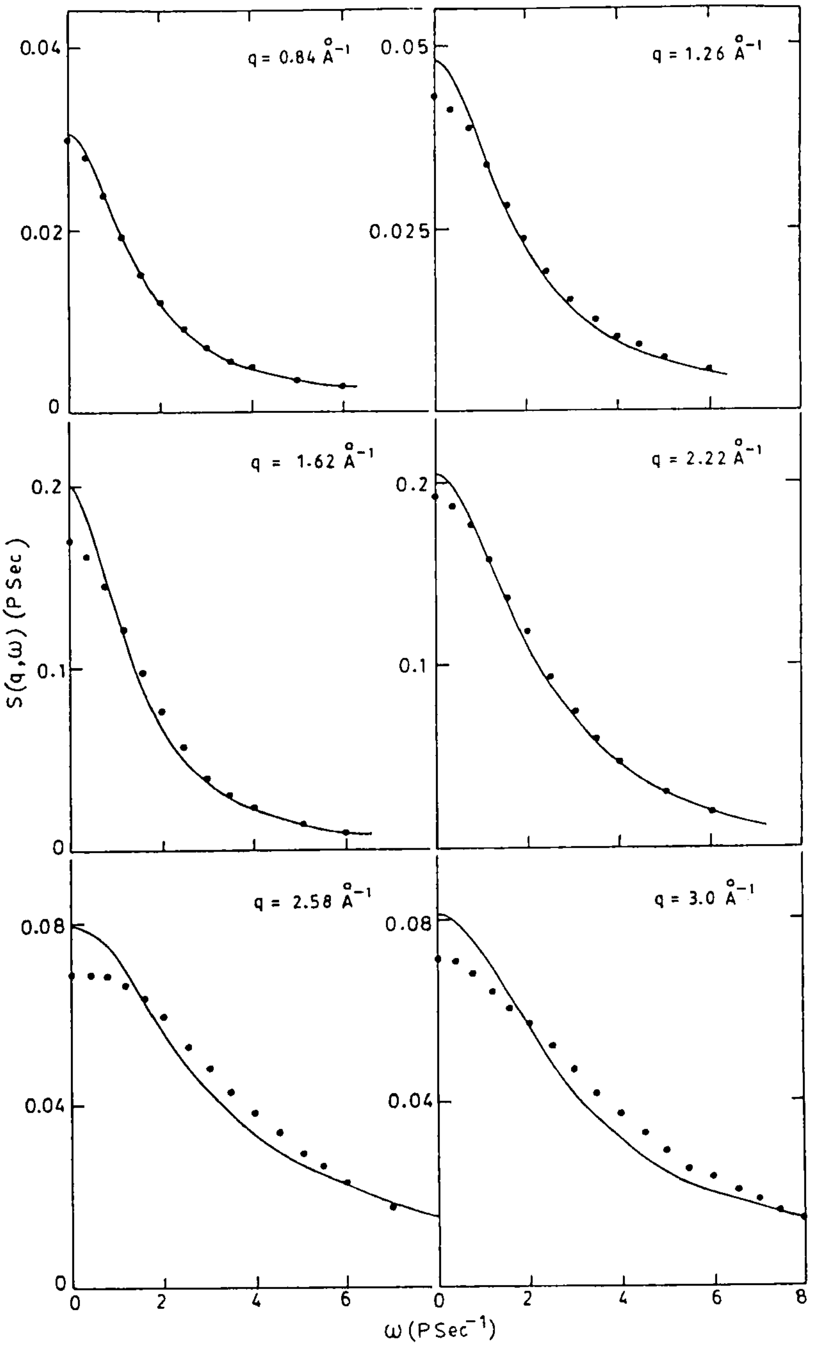

Figure 2 The variation of the dynamical structure factor $S(q, \omega)$ for Argon fluid with ω at $T^* = 0.974$ and $n^* = 0.668$ for different values of q (given in each part). Dots represent neutron scattering data and continuous lines represent our results.

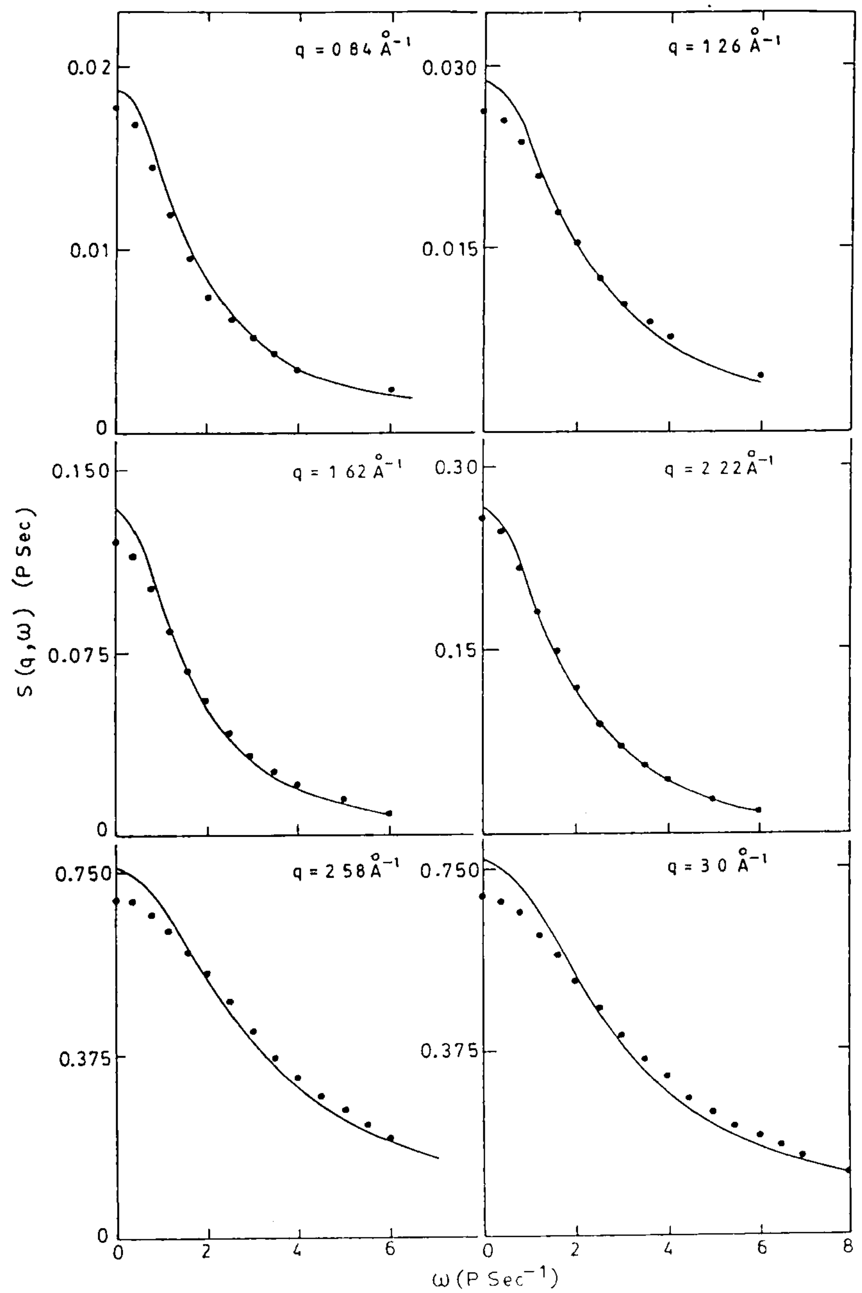

Figure 3 Same as Figure 2 but at $n^* = 0.763$.

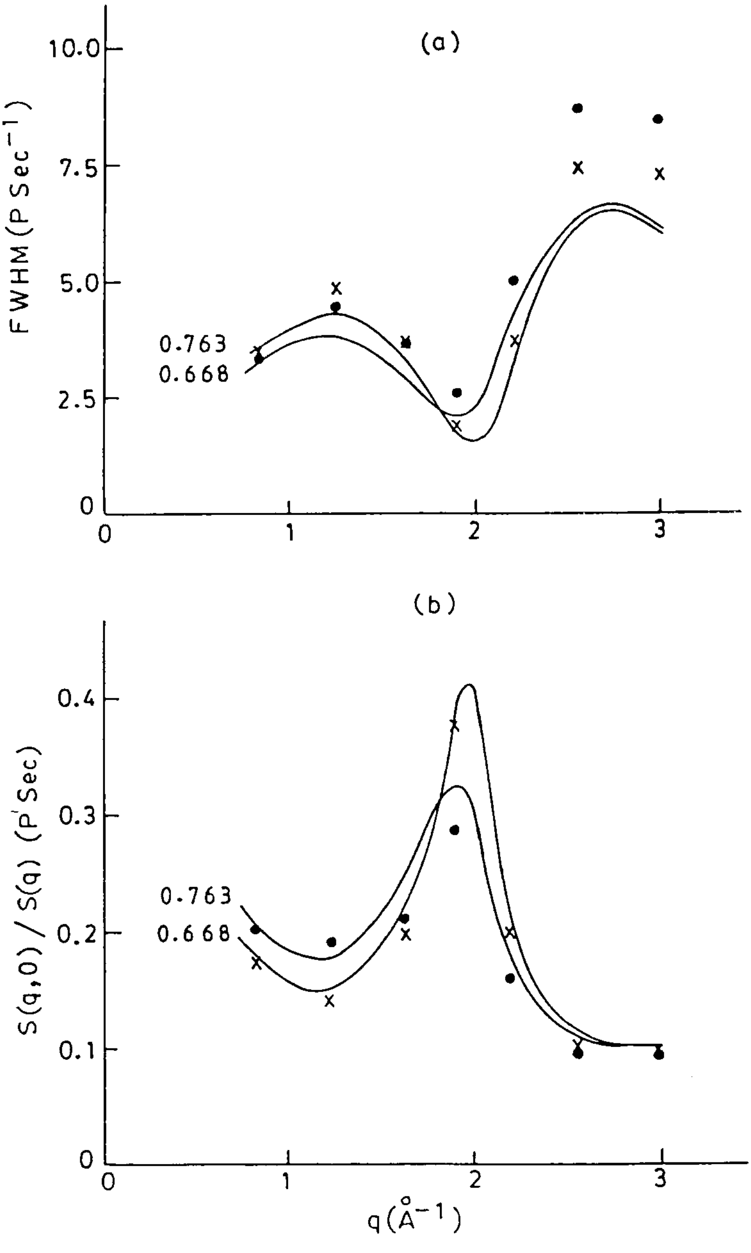

Figure 4 Variation of FWHM of $S(q, \omega)$ and $S(q, 0)/S(q)$ with q. Dots and crosses represent neutron scattering data at $n^* = 0.668$ and 0.763, respectively.

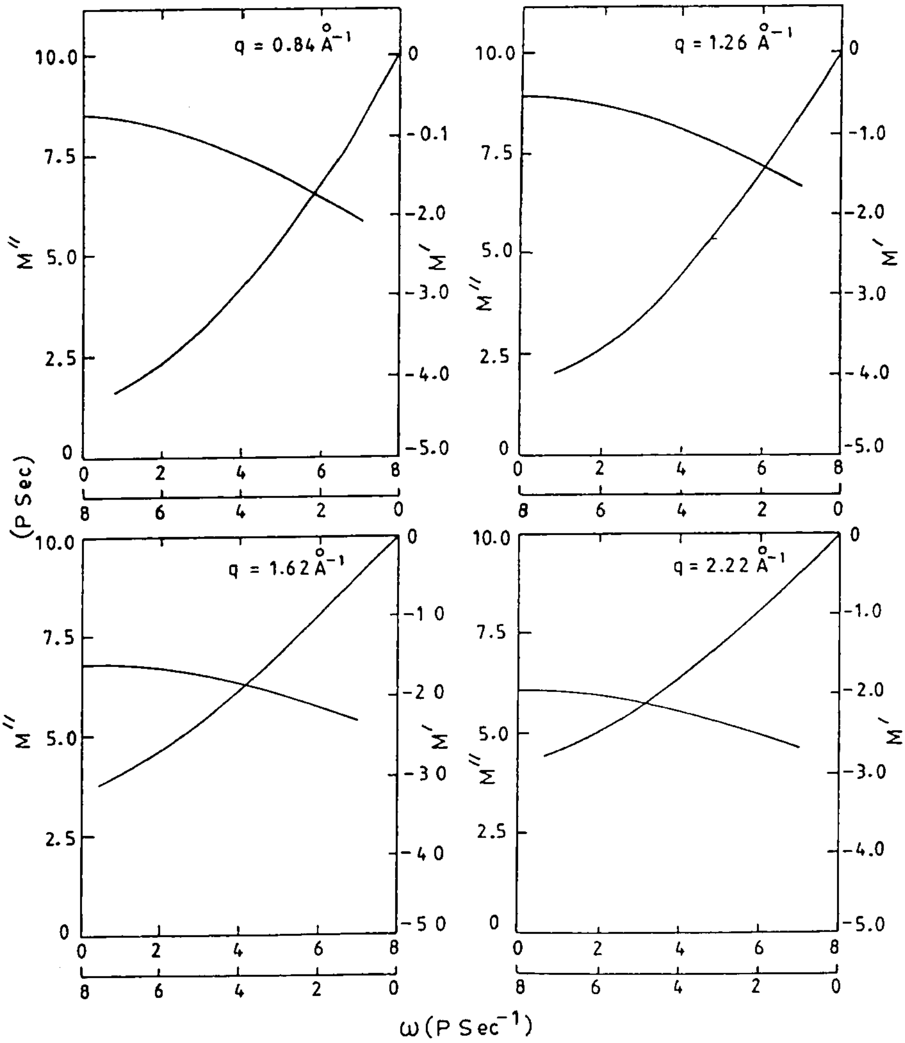

Figure 5 Variation of real part $M_2'(q, \omega)$ and imaginary part $M_2''(q, \omega)$ of the memory function with ω. The scale for ω for M_2' runs from right to left and that for M_2'' in the reverse direction (shown by the doubled scale).

appears explicitly in the expression of $S(q, \omega)$. For small ω the expansion of $M_2'(q, \omega)$ and $M_2''(q, \omega)$ are given as

$$M_2'(q, \omega) = \frac{a\omega}{4b^2}\left[\pi^2 - \sum_{k=0}^{\infty}(\tfrac{1}{4} + k)^2\right] - \left(\frac{\pi\omega}{2b}\right)^3 \frac{\pi a}{6b} \tag{14a}$$

and

$$M_2''(q, \omega) = \frac{\pi a}{2b}\left[1 - \frac{1}{2}\left(\frac{\pi\omega}{2b}\right)^2 + \frac{5}{24}\left(\frac{\pi\omega}{2b}\right)^4 - \cdots\right]. \tag{14b}$$

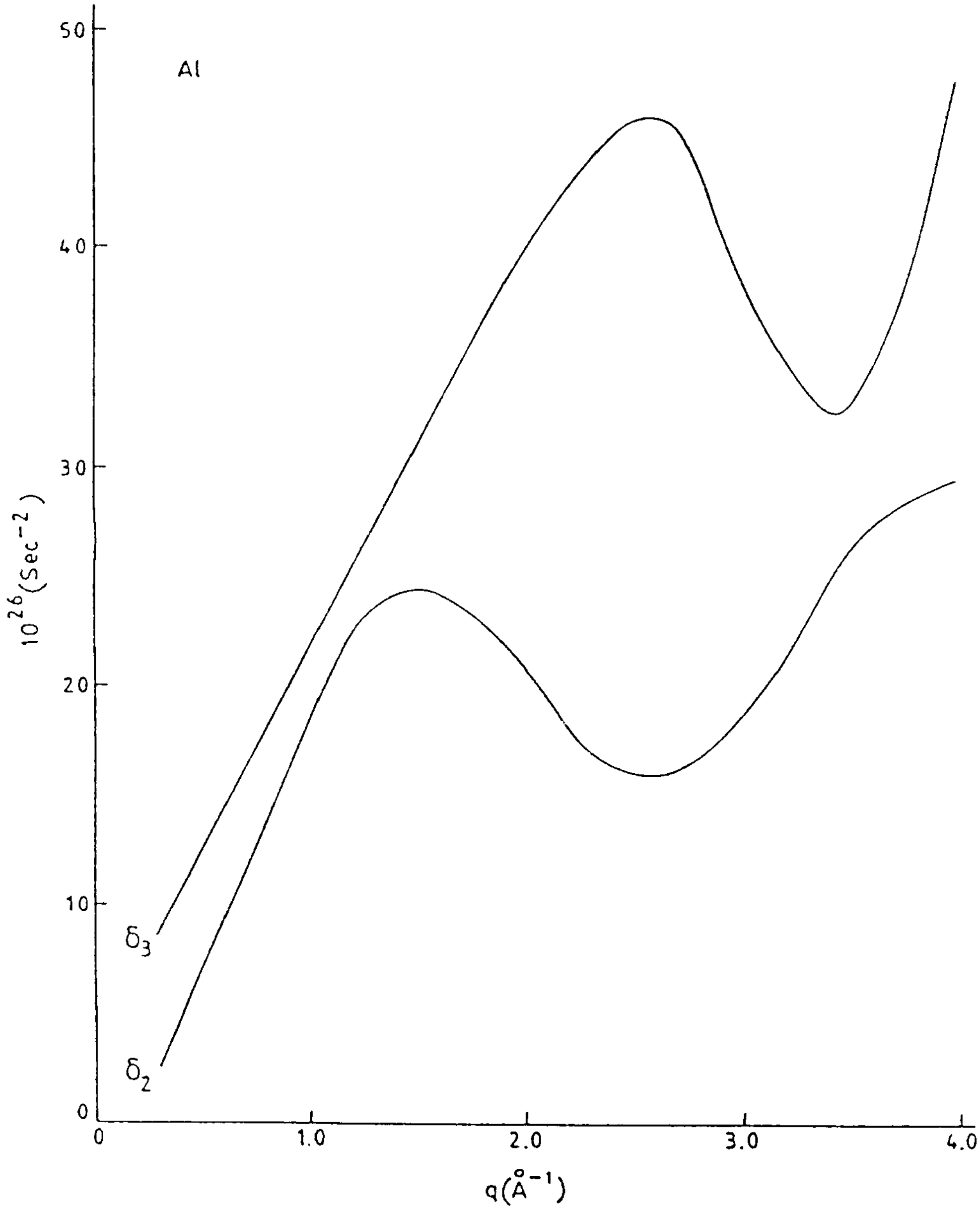

Figure 6 Same as Figure 1 but for liquid aluminium at its triple point.

Using above expansions in Eq. (7), one gets for the low frequency behaviour of $M_1(q, \omega)$ given as

$$M_1''(q, \omega) = \delta_1 \left(\frac{2b}{\pi a}\right)\left[1 + \frac{\pi^2\omega^2}{8b^2}\left(1 - 2\left(\frac{4b^2}{\pi^2 a} + 1 - \frac{16}{\pi^2}\right)^4\right)\right] \tag{15}$$

on the other hand,

$$M_2'(q, \omega) = \frac{\pi a}{2b} - \frac{a}{2b}\sum_{k=0}^{\infty} \frac{1}{\frac{\omega}{4b} + \frac{(\frac{1}{4} + k)^2}{\omega} 4b} \tag{16a}$$

and

$$M_2''(q, \omega) = \frac{\pi a}{2b} \exp\left(-\frac{\pi\omega}{2b}\right), \tag{16b}$$

for large ω. These when substituted in Eq. (7), we get

$$M_1''(q, \omega) = \delta_1 \frac{\pi a}{2b} \frac{\exp(-\pi\omega/2b)}{\omega^2}. \tag{17}$$

It can be seen from Eqs (15) and (17) that $M_1''(q, \omega)$ will have a maximum for $b^2/a (= \delta_3/\delta_2) < 3.277$. We have plotted δ_2 and δ_3 of liquid aluminium in Figure 6 for the comparison with results of argon shown in Figure 1. It is clearly seen from Figure (6) and Figure (1) that this ratio (δ_3/δ_2) is close to 1.25 for liquid aluminium and is about 2.25 for fluid Ar for small q, where collective behaviour is dominated. This leads to the more pronounced peak in $M_1''(q, \omega)$ for liquid aluminium than that in fluid Ar. This and the present results for fluid Ar and our earlier results[3] for liquid aluminium of $S(q, \omega)$ suggest that collective peak in $S(q, \omega)$ appears when there exist strong peak in $M_1''(q, \omega)$ which depends on the ratio δ_3/δ_2. The difference in value if δ_3/δ_2 for liquid Al and Ar implies that Al is more harmonic like whereas Ar is more anharmonic system. This ratio is roughly related to Grüneisen parameter used in the discussion of anharmonicity in solids.

4 CONCLUSION

In this paper we have calculated $S(q, \omega)$ of fluid Ar^{36} using secant hyperbolic form of the memory function appearing in the Mori–Zwanzig formalism. The results are compared with neutron scattering data and are found to be in good agreement for wave number $q \leq 2.5$ Å^{-1}. From the good agreement obtained here as well as from our earlier work[3] on the dynamical structure factor of liquid aluminium, we find that secant hyperbolic form of the memory function provides a good representation for small and intermediate wave number.

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APPENDIX

Expression for Ω_l^4:

The expression for the fourth frequency sum rule of longitudinal current current correlation function has been obtained to be

$$\Omega_l^4(q) = 15q^4\left(\frac{k_BT}{m}\right)^2 + \frac{nk_BT}{m^2}\int d\mathbf{r}_1 g(r_1)[15q^2U_{1xx}$$
$$+ 6q^3\sin(qx_1)U_{1x\alpha\alpha} + 2(k_BT)^{-1}(1-\cos(qx_1))U_{1x\alpha}^2]$$
$$+ \frac{n^2}{m^2}\iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2)[\{1 - 2\cos(qx_1)\}$$
$$+ \cos(q(x_1 - x_2))]U_{1x\alpha}U_{2x\alpha} \tag{A.1}$$

In above equation $g(r_1)$ and $g_3(\mathbf{r}_1, \mathbf{r}_2)$ are static pair and triplet correlation function and the wave vector $\mathbf{q}$ is assumed to be along x-axis. We have used the notation

$$U_{1\alpha\beta} = \frac{\partial^2 U(r_1)}{\partial r_{1\alpha}\partial r_{1\beta}} \quad \text{and} \quad U_{1\alpha\beta\gamma} = \frac{\partial^3 U(r_1)}{\partial r_{1\alpha}\partial r_{1\beta}\partial r_{1\gamma}} \tag{A.2}$$

The subscript 2 and U represent that the argument of interaction potential $U(r_1)$ is changed to r_2. Using the relations for the derivatives of the central potential, namely

$$U_{1\alpha\beta} = A_1 r_{1\alpha} r_{1\beta} + B_1\delta_{\alpha\beta} \tag{A.3}$$

and

$$U_{1\alpha\beta\gamma} = C_1 r_{1\alpha} r_{1\beta} r_{1\gamma} + A_1(r_{1\alpha}\delta_{\beta\gamma} + r_{1\beta}\delta_{\alpha\gamma} + r_{1\gamma}\delta_{\alpha\beta}) \tag{A.4}$$

where

$$B_1 = \frac{1}{r_1}\frac{dU(r_1)}{dr_1},\ A_1 = \frac{1}{r_1}\frac{dB_1}{dr_1} \quad \text{and} \quad C_1 = \frac{1}{r_1}\frac{\partial A_1}{\partial r_1} \tag{A.5}$$

it is straight forward to carry out the angular integration of the pair contribution terms in Eq. (A.1). The result is

$$\Omega_{l2}^4 = \frac{4\pi nk_BT}{3m^2}\int_0^\infty dr_1 r_1^2 g(r_1)[15q^2(A_1r_1^2 + 3B_1)$$
$$+ 18q(3j_1A_1r_1 + (j_1 - 2J_2)C_1r_1^3 + 2(k_BT)^{-1}(3B_1^2(1 - j_0) + A_1r_1^2(A_1r_1^2 + 3B_1)$$
$$\times (1 - 3j_0 + 6J_1))] \tag{A.6}$$

In Eq. (A.6) j_0, j_1, j_2 are spherical Bessel functions of zeroth, first and second order; their arguments qr is suppressed for convenience. Also $J_1 = j_1/qr$ and $J_2 = j_2/qr$.

The angular integration of the triplet contribution term given in the curly bracket of Eq. (A.1) is straight forward. This can be done by expanding $g_3(\mathbf{r}_1, \mathbf{r}_2)$ which is a function of r_1, r_2 and β i.e. the cosine of the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, in terms of spherical harmonics $Y_{lm}(\theta, \phi)$ in the following way,

$$g_3(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l=0}^{\infty} \sum_{m=-1}^{1} \frac{4\pi}{2l+1} g^l(r_1, r_2) Y^*_{lm}(\theta_2, \phi_2) Y_{lm}(\theta_1, \phi_1) \tag{A.7}$$

where (θ_1, φ_1) and (θ_2, ϕ_2) are the polar angles of $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. The coefficient $g^l(r_1, r_2)$ can be obtained from the relation

$$g^l(r_1, r_2) = \frac{2l+1}{2} \int_{-1}^{1} d\beta P_l(\beta) g_3(\mathbf{r}_1, \mathbf{r}_2) \tag{A.8}$$

where $P_l(\beta)$ is Legendre polynomial of order l.

The angular integration of the last term in Eq. (A.1) is quite tricky. For this term it is of no use to expand $g_3(\mathbf{r}_1, \mathbf{r}_2)$ using Eq. (A.7) as $\cos(q(x_1 - x_2))$ involves the angles between $\mathbf{q}$ and both $\mathbf{r}_1$ and $\mathbf{r}_2$. However it is possible to get rid of this difficulty with the help of symmetric properties of the derivaties of central potential as described below:

Using

$$\frac{\partial U(r_{jk})}{\partial r_{j\alpha} \partial r_{j\beta}} = \frac{\partial U(r_{kj})}{\partial r_{j\alpha} \partial r_{j\beta}} = -\frac{\partial U(r_{jk})}{\partial r_{j\alpha} \partial r_{k\beta}} = \frac{\partial U(r_{jk})}{\partial r_{jk\alpha} \partial r_{jk\beta}} \frac{\partial r_{jk\alpha}}{\partial r_{j\alpha}} \frac{\partial r_{jk\beta}}{\partial r_{j\beta}} \tag{A.9}$$

and the defination of $g_3(\mathbf{r}_1, \mathbf{r}_2)$ i.e.

$$n^3 g_3(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j \neq k} \langle \delta(\mathbf{r}_1 - \mathbf{r}_k + \mathbf{r}_j) \delta(\mathbf{r}_2 - \mathbf{r}_1 + \mathbf{r}_j) \rangle. \tag{A.10}$$

We rewrite the last term in Eq. (A.1) in an equivalent form

$$T = \sum_{i \neq j \neq k} \left\langle \cos(q x_{ik}) \frac{\partial^2 U(r_{jk})}{\partial r_{j\alpha} \partial r_{jx}} \frac{\partial^2 U(r_{ji})}{\partial r_{j\alpha} \partial r_{jx}} \right\rangle. \tag{A.11}$$

Making an interchanging of the atom i and j and using the property (A.9), Eq. (A.11) can be written in an alternative form

$$T = n^2 \iint g_3(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \cos(q x_1) U_{12x\alpha} U_{2x\alpha} \tag{A.12}$$

with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| = |(\mathbf{r}_i - \mathbf{r}_k) - (\mathbf{r}_i - \mathbf{r}_j)|$.

The subscript 12 on U in Eq. (A.12) and in what follows represents that the argument of potential $U(\mathbf{r}_1)$ is changed to $\mathbf{r}_{12}$. We have thus transferred the angle of $\mathbf{r}_1$ and $\mathbf{r}_2$ from $\cos(q(x_1 - x_2))$ to the derivative of the potential. Now we define a new function

$$F(\beta) = g_3(\mathbf{r}_1, \mathbf{r}_2) U_{12x\alpha} \tag{A.13}$$

which is a function of β and can easily be expanded in terms of spherical harmonics. Using the expansion procedure and after a lengthy algebra, the result obtained for the triplet contribution is given by

$$\begin{aligned}\Omega_{l3}^4 = \frac{8\pi^2 n^2}{3m^2} \iint_0^\infty dr_1 dr_2 r_1^2 r_2^2 \int_{-1}^{1} d\beta g_3(\mathbf{r}_1, \mathbf{r}_2)[(A_1 A_2 r_1^2 r_2^2 \beta^2 \\ + 2A_1 B_2 r_1^2 + 3B_1 B_2) - 6\{\theta_1(\beta^2 A_1 A_2 r_1^2 r_2^2 + A_2 B_1 r_2^2) \\ + (\theta_2 \beta^2 + J_1) B_1 A_2 r_2^2 + j_0 B_1 B_2\} + 3\{\beta_2 A_2 A_{12} r_{12}^2 \\ \times (\theta_1 \beta_1 r_1 - (\theta_2 \beta^2 + J_1)/r_{12} + A_{12} B_2 r_{12}^2 (\theta_1 r_1 \\ \times (r_1 - 2\beta r_2) + (\theta_2 \beta^2 + J_1) r_2^2)/r_{12}^2 + (\theta_2 \beta^2 + J_1) \\ \times A_2 B_{12} R_2^2 + j_0 B_1 B_{12}\}],\end{aligned} \tag{A.14}$$

where

$$\theta_1 = j_0 - 2J_1;\ \theta_2 = \theta_1 - J_1$$

The variables β_1 and β_2 are respectively, the cosine of the angles between the vectors $\mathbf{r}_1$ and $\mathbf{r}_{12}$ and $\mathbf{r}_2$ and $\mathbf{r}_{12}$. We would like to mention that arguments leading to simplification of triplet contribution are different than the first given by Bansal and Pathak[11]. However, our result agrees with their result.

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