© *Proc. Indian natn. Sci. Acad.*, **48**, A, No. 2, 1982, pp. 167–171
Printed in India.
Fluid Physics

FOURTH MOMENT OF COHERENT SCATTERING FUNCTION

P. K. CHAKRABARTI
Physics Department, St. Xaviers' College, 30 Park Street, Calcutta-700 016, India
and
T. NAMMALVAR
Physics Department, Rajah's College, Bobbili-532 558, India
and
R. C. SASTRI
Physics Department, Jadavpur University, Calcutta-700 032, India

(*Received 8 June 1981*)

The longitudinal frequency ω_l which is the square root of the ratio of the fourth and second moments of the coherent scattering function has been calculated for liquid rubidium using square well type interaction. Structural features in ω_l are reported that closely follow Rahman's simulation result.

Keywords: Coherent Scattering Function; Fourth Moment; Pair Correlation Function; Simulation Result; Structural Features; Square Well

INTRODUCTION

IT is well established that many experimental intricacies creep in the measurement of the fourth moment $\langle \omega^4 \rangle$ at low momentum and large energy transfers because of the considerable errors in the wings of the scattering function $s(k, \omega)$. Under such circumstances, some alternative methods for $\langle \omega^4 \rangle$ are essential to circumvent such difficulties. Recent studies (Hubbard & Beeby, 1969; and Bansal *et al.*, 1978) give a calculation of this function for a Lennard-Jones fluid under certain approximation. In the present work, the authors have obtained simple analytic expressions for ω_l using a square-well (*sw*) model that can be computed with less computational efforts and furthermore there is no approximation introduced in the evaluation of the function.

THEORY

Many aspects of the k (wave vector) and ω (frequency) behaviour of the scattering can be inferred from their generalised low order moments which may be written as

$$\langle \omega^m \rangle = \int_{-\infty}^{\infty} \omega^m s(k, \omega) d\omega \Big/ \int_{-\infty}^{\infty} s(k, \omega)\, d\omega$$

where $s(k, \omega)$ describes their longitudinal motion in terms of the particle density.

Explicit expressions upto eight moments are available (Forster *et al.*, 1968; and Bansal & Pathak, 1974). The fourth moment for the coherent scattering denoted by ω_l is (Ailawadi, 1980; and Copley & Lovesey, 1975),

$$\omega_l^2 \equiv \langle \omega_c^4 \rangle / \langle \omega_c^2 \rangle$$

$$= \frac{3k^2}{m\beta} + \frac{\rho}{m}\int g(r)\,(\bar{k}\cdot\bar{\nabla})^2\, u(r)\, d\bar{r} - \frac{\rho}{m}\int g(r)\cos(\bar{k}\cdot\bar{r})\,(\bar{k}\cdot\bar{\nabla})^2\, u(r)\, d\bar{r} \quad \ldots(1)$$

Here $g(r)$ is the pair correlation function (PCF), $u(r)$ is the potential under consideration, ρ is the number density and the rest of the symbols have their usual significance.

After performing the required differentiation and angular integration, respectively, in the second and third terms on the right hand side of Eqn. (1) we get,

$$\omega_l^2 = \frac{3k^2}{m\beta} + \frac{4\pi\rho}{3m}\int_0^\infty \frac{d}{dr}\left(r^2\frac{du}{dr}\right) g(r)\, dr - \frac{4\pi\rho}{m}\int_0^\infty \left[u''\left(\frac{\sin kr}{kr} + \frac{2\cos kr}{(kr)^2} - \frac{2\sin kr}{(kr)^3}\right) - \frac{2u'}{r}\left(\frac{\cos kr}{(kr)^2} - \frac{\sin kr}{(kr)^3}\right)\right] r^2 g(r)\, dr \quad \ldots(2)$$

The evaluation of the integrals in eqn. (2) using the model is straight forward and is given in the Appendix at the end of the text.

We write the resulting equation as

$$\omega_l^2 = \frac{3k^2}{m\beta} + T_2 - T_3 \quad \ldots(3)$$

Results and Discussion

In the present calculation, the value of $\sigma = 4.306$Å is the best chosen to fit both static (Chakrabarti & Sastri, 1981) and dynamic properties near the melting temperature. The frequency calculated from eqn. (3) is shown in the figure. Hubbard & Beeby (1969) in their calculation of the fourth moment $\langle\omega^4\rangle$ have approximated the product $r^2u''(r)\, g(r)$ by a delta function near the hard core radius R_0 and replaced the integral by a weight factor ω_E^2. Also they have neglected the term proportional to $u'(r)$ in eqn. (2). In our calculations with the $s\omega$ model we have seen that the integral containing the product $r^2u''(r)\ g(r)$ makes a contribution $0.57 \times 10^{13}\ s^{-1}$ that is comparable with the contribution $0.1 \times 10^{13}\ s^{-1}$ coming from the $u'(r)$ term. So we have incorporated all the terms in our calculation of the function ω_l^2. In the present context only the values of $g(r)$ at $r = \sigma, \lambda\sigma$ are needed for the evaluation of ω_l^2 thus avoiding the details and uncertainties involved in the $1O\omega$ low region of r. The structure factor $s(k)$ is also shown in the figure to observe the structural features of ω_l curve (Fig. 1). It is clear from the figure that the first minimum in ω_l and first peak of $s(k)$ differ only by 0.04Å^{-1} and the rest of the features closely follow that of Rahman's (1974) simulation result. Thus the $s\omega$ model satisfactorily represents the structural details of the fluids. We conclude with a suggestion that the transverse frequency mode can also be analysed in the same fashion.

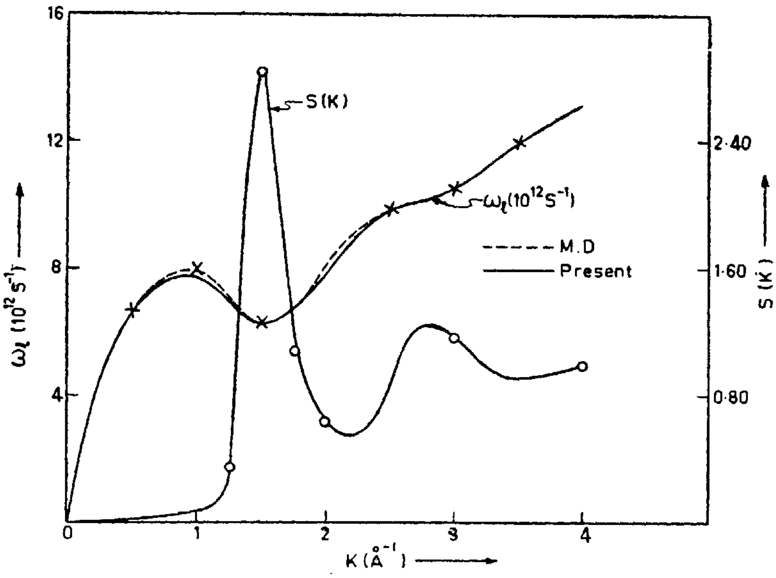

FIG. 1. ω_l calculated at $T = 313\ ^\circ$K from eqn. (3) for liquid rubidium as a function of $(K)\text{Å}^{-1}$. Solid curve denotes present work, ——— that of Rahman (1974). Structure factor $S(K)$ also shown in the figure.

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Appendix

For a square well fluid, the Boltzmann factor and the potential derivative respectively are given by

$$\begin{aligned} e^{-\beta u(r)} &= 0 \quad , \; r \leqslant \sigma \\ &= e^{\beta \epsilon} \quad , \; \sigma < r < \lambda\sigma \\ &= 1 \quad , \; r \geqslant \lambda\sigma \\ \frac{du(r)}{dr} &= -\infty , \; r = \sigma \\ &= \infty \quad , \; r = \lambda\sigma \\ &= 0 \quad , \; r \neq \sigma, \lambda\sigma \end{aligned} \qquad \ldots(1A)$$

Therefore, the integral in the second term of eqn. (2) can be written as

$$I = \int_0^\infty \frac{d}{dr}\left(r^2 \frac{du}{dr}\right) g(r)\, dr$$

Integrating by parts we get

$$I = r^2 g(r) \frac{du}{dr} \int_0^\infty - \int_0^\infty (r) g' r^2 \frac{du}{dr}\, dr \qquad \ldots(2A)$$

In view of properties of the potential derivative in (1A), the first term in (2A) vanishes.

Hence

$$I = -\int_0^\infty g'(r)\, r^2 \frac{du}{dr}\, dr$$

Now

$$\frac{d}{dr}\left(e^{-\beta u(r)}\right) = -\beta e^{-u(r)\beta} \frac{du}{dr}$$

$$\therefore \qquad I = \frac{1}{\beta} \int_0^\infty e^{\beta u(r)} g'(r)\, r^2 \frac{d}{dr}\left(e^{-\beta u(r)}\right) dr$$

The derivative of $e^{-\beta u(r)}$ is proportional to the Dirac delta-functions are $r = \sigma$ and $r = \lambda\sigma$. The integral I thus splits into two parts, one part for the range $r = 0$ to σ^+ and the other for $r = \sigma^+$ to ∞

$$r = 0 \text{ to } \sigma^+ : \frac{d}{dr}(e^{-\beta u(r)}) = e^{\beta\epsilon}\,\delta(r - \sigma)$$

$$r = \sigma^+ \text{ to } \infty : \frac{d}{dr}(e^{-\beta u(r)}) = (1 - e^{\beta\epsilon})\,\delta(r - \lambda\sigma)$$

Substituting these results into the integral I, we get,

$$I = \frac{\sigma^2}{\beta}[g'(\sigma^+) + (1 - e^{\beta\epsilon})\,g'(\lambda\sigma^+)\,\lambda^2]$$

where $g'(\sigma^+)$ i.e., the derivative of R.D.F. evaluated just inside the well and $g'(\lambda\sigma^+)$ evaluated just outside the well.

The integrals in the third term in eqn. (3) can also be evaluated exactly in the same way while

$$T_2 = \frac{4\pi\rho\sigma^2}{3m\beta}[g'(\sigma) + (1 - e^{\beta\epsilon})\,\lambda^2 g'(\lambda\sigma)]$$

$$T_3 = \frac{4\pi\rho}{m\beta}[I_1 + I_2 + I_3 + I_4]$$

Here

$$I_1 = [2\sigma g(\sigma) + \sigma^2 g'(\sigma)]\,\phi(\sigma)$$
$$I_2 = (1 - e^{\beta\epsilon})\,[2\lambda\sigma g(\lambda\sigma) + \lambda^2\sigma^2 g'(\lambda\sigma)]\,\phi(\lambda\sigma)$$
$$I_3 = \sigma^2\,[g\sigma)\,\phi'(\sigma) + (1 - e^{\beta\epsilon})\,\lambda^2 g(\lambda\sigma)\,\phi'(\lambda\sigma)]$$
$$I_4 = 2\sigma\,[g(\sigma)\,\phi_1(\sigma) + (1 - e^{\beta\epsilon})\,\lambda g(\lambda\sigma)\,\phi_1(\lambda\sigma)]$$

and

$$\phi(r) = \frac{\sin kr}{kr} + \frac{2\cos kr}{(kr)^2} - \frac{2\sin kr}{(kr)^3}$$

$$\phi_1(r) = \frac{\cos kr}{(kr)^2} - \frac{\sin kr}{(kr)^3}$$

In the above expression $\phi'(x)$ denotes the derivative of $\phi(r)$ with respect to r evaluated at x, ϵ and λ are the $s\omega$ parameters.