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Collective dynamics in liquid lithium, sodium, and aluminum

Shaminder Singh and K. Tankeshwar
Department of Physics, Panjab University, Chandigarh-160014, India

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Inelastic x-ray scattering data of liquid Li, Na, and Al for dynamical structure factors have been analyzed by proposing a semiempirical model. The model is based on the extension of the hydrodynamic model to the viscoelastic region so that it satisfies the first four nonvanishing sum rules. It has been found that the semiempirical model fits well with the x-ray scattering data for liquid metals investigated here. The physical meaning of the parameters is also discussed.

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The dynamical structure factor of a liquid contains information about the atomic motion at different time and length scales. Experimentally information at different length and time scales about dynamics of a liquid can be obtained by performing neutron or x-ray inelastic scattering. Recently, there has been increasing interest in the experimental investigation of the dynamical structure factor $S(q,\omega)$ due to its possibility of studying through x-ray inelastic scattering in the nonhydrodynamic region. Liquid metals like Al [1], Na [2], and Li [3] have been studied by x-ray inelastic scattering for which the scattering cross section is purely coherent. There exist theoretical methods to study the dynamical structure factor. One approach to studying the density-density correlator, a quantity directly related to $S(q,\omega)$, is based on Mori's equation of motion [4,5]. In this approach the most important quantity to be examined is the space-time memory function. In addition to the microscopic ways of evaluation [4–7], there exist models for the memory function involving single [4,8] and two relaxation times [9–11]. The single relaxation time models for the memory function have been able to explain the existence of collective density excitations in liquid metals. However, to reproduce completely the line shapes a limited success has been achieved, even if the parameters involved are best fitted to experimental data. For example, viscoelastic model could not reproduce x-ray scattering data of liquid Li [2]. The attempt [2] to fit the simple hydrodynamic formula also could not reproduce the x-ray scattering data of the dynamical structure factor in the nonhydrodynamic region. Therefore, Scopigno *et al.* [1–3] have followed two relaxation time (fast and slow) models to fit x-ray scattering data of liquid Li, Na, and Al. The origin of these two relaxation times, which is of significant importance, is not fully understood, especially the fast one. In the absence of a clear understanding about relaxation processes in these liquid metals and having experimental data now available for small wave number q, it appears useful to analyze the data by extending the hydrodynamic model to the viscoelastic region. Therefore, in the present work, we propose a model keeping in view that short time dynamics becomes more important in the viscoelastic region. The modification of the hydrodynamic formula for the density correlation function is done in such a way that it satisfies sum rules up to sixth order and has the expected Gaussian behavior for a free particle, but reduces to the hydrodynamic formula in its appropriate limit. The number of parameters in our proposed model is also same as the number of variables in the linear hydrodynamic formula. Therefore, the physical meaning of the parameters can also be investigated. The model has the possibility of predicting the dispersion gap as well. We have applied the model to study x-ray scattering data of $S(q,\omega)$ for liquid Li, Na, and Al at different wave numbers.

For a linearized symmetric hydrodynamic, density correlation function, $F(q,t)$ has the form

$$F(q\to 0,t)=S(q\to 0)[a\exp(-t/\tau_a)+(1-a)\times\exp(-t/\tau_b)\cos(\omega_0 t)], \tag{1}$$

where $S(q)$ is the static structure factor, $a=(\gamma-1)/\gamma$, $\tau_a=1/D_T q^2$, $\tau_b=1/\Gamma q^2$, and $\omega_0=cq$. Here D_T is thermal diffusivity, Γ is the sound wave damping constant, $\gamma=C_p/C_v$, and c is sound velocity. The dynamical structure factor defined by

$$S(q,\omega)=\frac{1}{\pi}\mathrm{Re}\int F(q,t)\exp(-i\omega t)dt$$

is then given by

$$S(q\to 0,\omega)=\frac{S(q)}{\pi}\left[\frac{\gamma-1}{\gamma}\frac{D_T q^2}{\omega^2+(D_T q^2)^2}+\frac{1}{2\gamma}\left(\frac{\Gamma q^2}{(\omega-cq)^2+(\Gamma q^2)^2}+\frac{\Gamma q^2}{(\omega+cq)^2+(\Gamma q^2)^2}\right)\right]. \tag{2}$$

This expression is valid in very small q region. Attempts have been made in the past to extend this to the viscoelastic region. Following the idea of McGreevy and Mitchel [12], in the present work we propose $F(q,t)$ to have the form

$$F(q,t)=S(q)[a\,\mathrm{sech}(t/\tau_1)+(1-a)\mathrm{sech}(t/\tau_2)\cos(\omega_O t)], \tag{3}$$

which has Gaussian behavior corresponding to a free particle for $t<\tau_1,\tau_2$, but reduces to Eq. (1) for t larger than τ_1 and τ_2. The expression for the dynamical structure factor is obtained to be

$$S_c(q,\omega)=S(q)\left\{\frac{a\tau_1}{2}\mathrm{sech}\left(\frac{\pi\omega\tau_1}{2}\right)+\frac{(1-a)\tau_2}{4}\left[\mathrm{sech}\left(\frac{\pi(\omega+\omega_0)\tau_2}{2}\right)+\mathrm{sech}\left(\frac{\pi(\omega-\omega_0)\tau_2}{2}\right)\right]\right\}. \quad (4)$$

Here the subscript c is used to differentiate it from the true experimental dynamical structure factor in which quantum aspects are associated. All the parameters of the model can be related to sum rules of $S(q,\omega)$ by the following relations:

$$\langle\omega^O\rangle=S(q), \quad (5)$$

$$\langle\omega^2\rangle=S(q)\left[\frac{a}{\tau_1^2}+(1-a)\omega_0^2+\frac{1-a}{\tau_2^2}\right], \quad (6)$$

$$\langle\omega^4\rangle=S(q)\left[\frac{5a}{\tau_1^4}+(1-a)\omega_0^4+\frac{6(1-a)\omega_0^2}{\tau_2^2}+\frac{5(1-a)}{\tau_2^4}\right], \quad (7)$$

and

$$\langle\omega^6\rangle=S(q)\left[\frac{61a}{\tau_1^6}+(1-a)\left(\frac{61}{\tau_2^6}+\omega_0^6+\frac{15\omega_0^4}{\tau_2^2}+\frac{75\omega_0^2}{\tau_2^4}\right)\right]. \quad (8)$$

$\langle\omega^0\rangle$, $\langle\omega^2\rangle$, $\langle\omega^4\rangle$, and $\langle\omega^6\rangle$ are the zeroth, second, fourth, and sixth sum rules of the dynamical structure factor, respectively. Expressions for these sum rules are already available [13] in terms of pair potential, static pair, and triplet correlation functions. If one chooses $\tau_1^2=\tau_2^2=m/q^2k_BT\alpha$ with $\langle\omega^2\rangle=q^2k_BT/m$, we obtain from Eq. (6)

$$\omega_0^2=\frac{q^2k_BT}{m(1-a)}\left[\frac{1}{S(q)}-\alpha\right], \quad (9)$$

which predicts a dispersion gap for $1/S(q)<\alpha$. Our model is different from McGreevy and Mitchell [12] in the sense that the number of parameters are same as those in the hydrodynamic model so that one can consider [15] them as their wave-vector-dependent equivalence.

We now apply the semiempirical model to the calculation of the dynamical structure factor of Li, Na, and Al for different wave numbers. Before we discuss the calculation procedure, it is worth noting that for comparing our results with experiments, we have used the approximation

$$S(q,\omega)=\frac{\beta\hbar\omega}{1-\exp(-\beta\hbar\omega)}S_c(q,\omega), \quad (10)$$

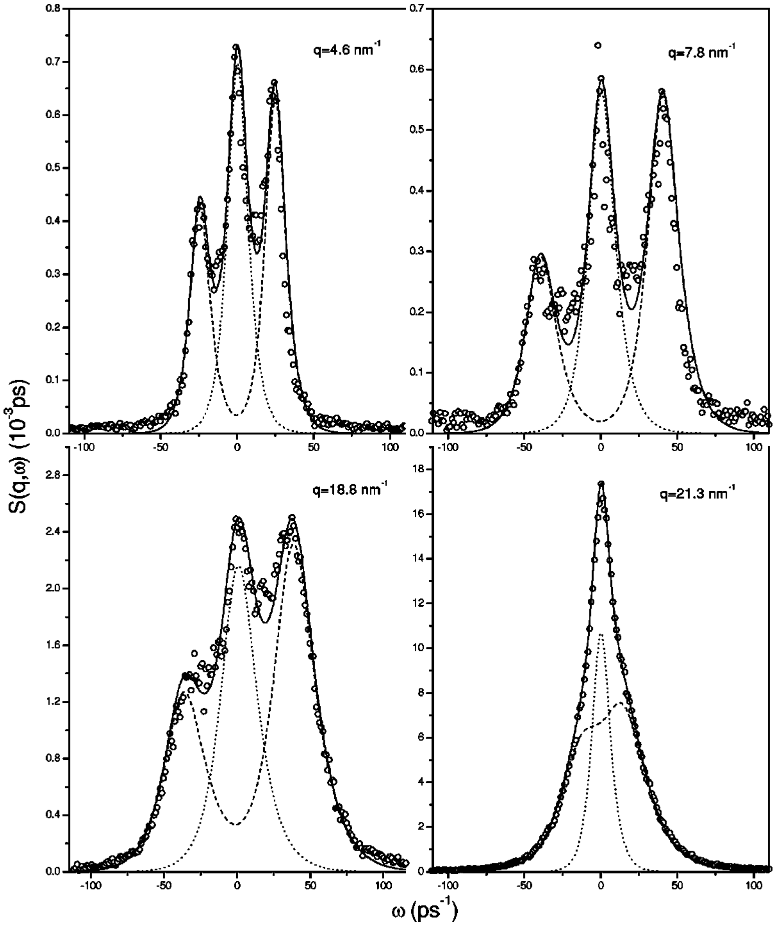

FIG. 1. Comparison of x-ray scattering data with results of our model for liquid Li at $T=475$ K for different wave numbers. Open circles are x-ray scattering data. Dotted lines with only a central peak are contributions of the first term, whereas dashed lines with only two side peaks are due to the contribution of last the two terms of Eq. (4). The sum of the two contributions is shown as a full line.

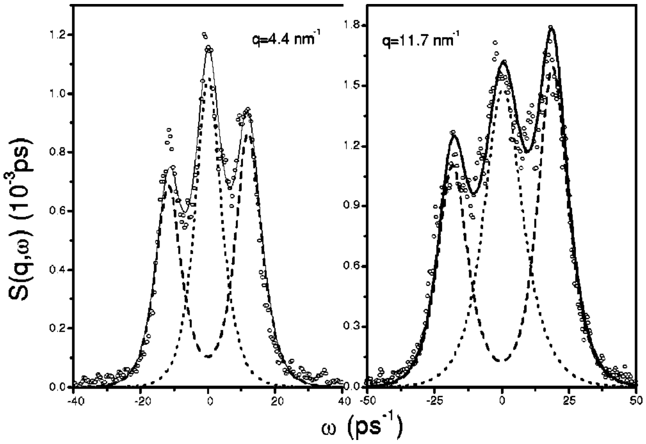

FIG. 2. Comparison of x-ray scattering data with predictions of Eq. (4) for liquid Na at $T=390$ K. Symbols are the same as that in Fig. 1.

which connects [2] the experimental dynamical structure factor to the classical counterpart $S_c(q,\omega)$. Here $\beta=1/k_BT$ and $\hbar$ is Planck's constant. In this work, we have used our empirical formula (4) for $S_c(q,\omega)$ with $S(q)$ taken from the experimental results and have fitted relaxation times, τ_1, τ_2, frequency ω_0, and a measuring the strength of viscous channel. We have studied the Al system at $T=1000$ K, Li at $T=475$ K and Na at $T=390$ K for different wave numbers. Results obtained for Li are shown in Fig. 1, for liquid Na in Fig. 2, and for liquid Al in Fig. 3 for a few wave numbers. The diffusive and collective mode contributions are shown separately in these figures. The dotted lines with a single peak are the contribution of the first term (diffusive) whereas dashed lines with two peak structures are the contribution of last two terms (collective) of Eq. (4). The full line with one central peak and two side peaks is representing the sum of two contributions. It can be seen from the Figs. 1–3 that our proposed model is able to provide a good agreement with x-ray scattering data of $S(q,\omega)$ for liquids Li, Na, and Al for all wave numbers. It is also seen from the figures that the sharpness of the two side peaks decreases with an increase in q, implying the reduction of collective effects. The two side peaks disappears at $q=q_m$, q_m is the wave number, where $S(q)$ has first maxima, implying the crossover from elastic to viscous behavior of fluid.

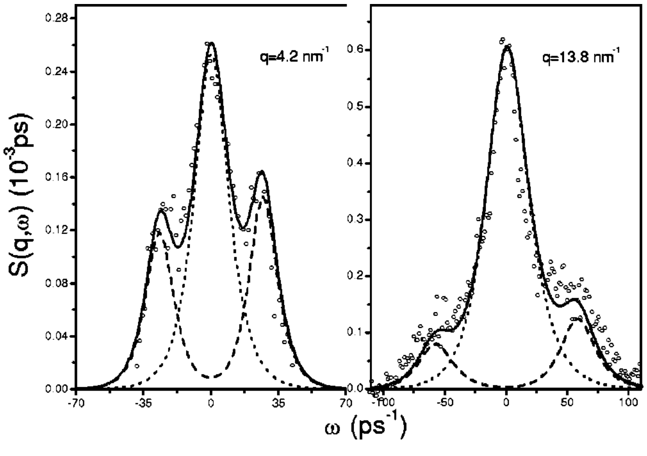

FIG. 3. Comparison of x-ray scattering data with predictions of Eq. (4) for liquid Al at $T=1000$ K. Symbols are the same as that in Fig. 1.

Since, in the limiting case the two relaxation times τ_1 and τ_2 have the same meaning as diffusive and viscous relaxations of the hydrodynamic model. Therefore, it is interesting to study the behavior of $1/\tau_1q^2$ and $1/\tau_2q^2$ with an increase in q, which should demonstrate the wave number dependence of thermal diffusivity, D_T and damping Γ, respectively. In Fig. 4 we have plotted $1/\tau_1q^2$ and $1/\tau_2q^2$ versus q. It can be seen that both $1/\tau_1q^2$ and $1/\tau_2q^2$ decrease with q. It can also be noted that the value of $1/\tau_1q^2$ is of the order of 10^{-6} m^2 s^{-1} which is typically of the same order as that of diffusivity. The experimental values of D_T [14] at $q=0$ are 18.79×10^{-6} m^2 s^{-1}, 66.77×10^{-6} m^2 s^{-1}, and 33.39×10^{-6} m^2 s^{-1} for Li, Na, and Al, respectively. On the other hand, damping Γ can be related to longitudinal viscosity and thermal conductivity of the system by the relation given as

$$\Gamma=\frac{1}{2\rho}\left[\frac{4}{3}\eta_s+\eta_B+(\gamma-1)\lambda/C_p\right], \qquad (11)$$

where ρ, η_s, η_B, λ, and C_p are mass density, shear viscosity, bulk viscosity, thermal conductivity, and specific heat at constant pressure, respectively. It is known [16] that the main contribution to Γ comes from the viscous processes. The values of $1/\tau_2q^2$ are of the same order as that of Γ when calculated from Eq. (11). For example, for Na, the value of Γ calculated from Eq. (11) by using the experimental values η_s, η_B, γ, λ, and C_p [14] is 5.4267×10^{-6} m^2 s^{-1}. Further, a decrease in $1/\tau_2q^2$ [or $\Gamma(q)$] is also similar to the behavior of generalized longitudinal viscosity with q, as observed in liquids [17,18].

The parameter a is also plotted in Fig. 4. It can be seen from the figure that a, which measures the strength of viscous channel in comparison to contribution due to diffusive phenonmena, is comparatively less in the case of Li and Na than in Al. This implies that collective motion is more pronounced in Li and Na than in Al. The values of a as predicted from hydrodynamical formula $[(\gamma-1)/\gamma]$ are 0.12, 0.10, 0.20 for Li, Na, and Al, respectively, at $q=0$ and are shown in Fig. 4 as horizontal arrows. It is also interesting to see that where collective density excitations are not clearly seen as side peaks in $S(q,\omega)$, our model shows the presence of collective modes. This is clearly demonstrated in Fig. 1, in the case of Li at $q=21.3$ nm^{-1}.

In Fig. 4 we have also shown a variation of ω_0 with q for three liquids considered here. The comparison is made with experimental results of dispersion curve. It is seen that a variation of ω_0 with q is that of the dispersion curve and is in good agreement with the experimental data. It is also noted that ω_0 shows linear behavior for small q values. The experimental values of sound velocity are 4450 m s^{-1}, 2500 m s^{-1}, and 4750 m s^{-1} for Li, Na, and Al, respectively. The experimental values of velocity are shown as a slope of lines in Fig. 4. It can be seen that the agreement is quite reasonable.

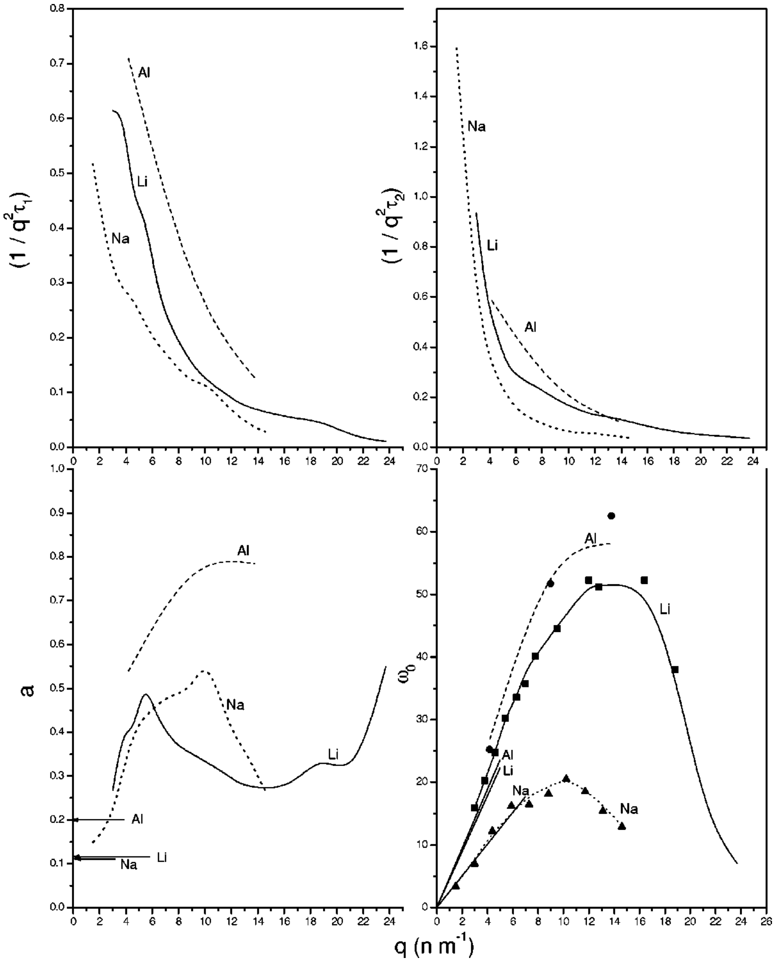

FIG. 4. $(1/\tau_1 q^2)$ in units of 10^{-6} m^2 s^{-1}, $1/\tau_2 q^2$ in units of 10^{-6} m^2 s^{-1}, ω_0 in units of ps^{-1}, and parameter a versus q. Solid lines are for Li, dotted lines are for Na, and dashed lines are for Al. Squares, triangles, and circles are experimental results of ω_0 for liquid Li, Na, and Al, respectively. Arrows represent the values of a $[=(\gamma-1)/\gamma]$ calculated from the experimental values of γ at $q=0$.

In conclusion we find that a simple modification of the hydrodynamic formula can be used to extend it to the viscoelastic region. The present proposed modification allows us to satisfy sum rules up to the sixth order and retain, in their respective limits, hydrodynamic and free particle results. The fitted parameters suggest that wave-number-dependent transport processes enter in the relaxation mechanism. The predictions of our model in agreement with the x-ray scattering data for three metals demonstrates the utility of the proposed modification of the hydrodynamic formula.

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