

**Reply to ‘‘Comment on ‘Collective dynamics in liquid lithium, sodium, and aluminum’’’’**

Shaminder Singh and K. Tankeshwar

*Department of Physics, Panjab University, Chandigarh 160014, India*

(Received 30 November 2003; published 21 July 2004)

Scopigno and Ruocco [Phys. Rev. E **70**, 013201 (2004)] have raised certain objections to physical interpretation of the parameters of the model proposed by us earlier [Singh and Tankeshwar, Phys. Rev. E **67**, 012201 (2003)]. We have found that heat diffusion term enters into processes which are responsible for the quasielastic peak of the dynamical structure factor. An attempt has been made to study the role played by atomic and electronic contributions to thermal conductivity for studying atomic density-density correlation function.

DOI: 10.1103/PhysRevE.70.013202

PACS number(s): 61.20.-p, 67.55.Jd, 61.25.Mv

We have extended [1] the hydrodynamic model for the calculation of the dynamical structure factor,  $S(q, \omega)$ , to the viscoelastic region by replacing the exponential term by the hyperbolic secant function. The model proposed by us reproduces experimental spectra of liquid metals Li, Na, and Al to a good level of accuracy, which is well received by the commenting authors. The functional form of the model proposed by us can be made to satisfy exactly the moments up to sixth order in addition to having all spectral moments finite. Scopigno and Ruocco (SR) have raised certain objections to the physical interpretation of parameters involved in our model, specifically concerning the quasielastic peak. We have attributed the quasielastic peak mainly to thermal relaxation, whereas SR relates it mainly to viscous processes [2–7]. Their interpretation assumes that thermal conductivity of liquid metals is three orders of magnitude more than the nonconducting liquids. In the present Reply, we have attempted to study the role being played by ionic and electronic contribution to thermal conductivity, which may justify our interpretation of the parameters of the model. Further, SR have argued that the hydrodynamic model cannot be applied to conducting liquids. However, the analysis given below suggests that if only the atomic contribution to the thermal conductivity is taken into account, one could apply the hydrodynamic formula to study the dynamical structure factor of liquid metals as well.

The dynamical structure factor  $S(q, \omega)$  [8] is defined as

$$S(q, \omega) = \int_{-\infty}^{\infty} \exp(-i\omega t) F(q, t) dt, \quad (1)$$

where  $F(q, t)$  is the intermediate scattering function and is defined as

$$F(q, t) = \langle n_q^*(0) n_q(t) \rangle - n(2\pi)^3 \delta(q), \quad (2)$$

with

$$n_q(t) = \frac{1}{\sqrt{N}} \sum_j \exp[iqR_j(t)]. \quad (3)$$

In the above equations,  $R_j$  is the position of the  $j$ th particle and  $n_q(t)$  is the Fourier transform of the number density defined as

$$n(\mathbf{r}, t) = \frac{1}{\sqrt{N}} \sum_j \delta(\mathbf{r} - R_j(t)). \quad (4)$$

The  $n(\mathbf{r}, t)$  satisfies the continuity equation [9] given by

$$\dot{n}(\mathbf{r}, t) + \frac{1}{m} \nabla \cdot \mathbf{p}(\mathbf{r}, t) = 0, \quad (5)$$

where  $p(\mathbf{r}, t)$  is momentum density and satisfies the following equation:

$$\dot{p}(\mathbf{r}, t) + \nabla \cdot \sigma(\mathbf{r}, t) = 0, \quad (6)$$

with  $\sigma(\mathbf{r}, t)$  as a stress tensor. Another equation of interest is

$$\dot{e}(\mathbf{r}, t) + \nabla \cdot \mathbf{j}^e(\mathbf{r}, t) = 0, \quad (7)$$

where  $e(\mathbf{r}, t)$  is energy density and  $\mathbf{j}^e(\mathbf{r}, t)$  is energy current. The Fourier transform of Eq. (7) results [9] in the component of  $J_q^e$  in the direction of  $q$  given as

$$-iqJ_q^{ez} = \dot{e}_q = \frac{d}{dt} \sum_i \left[ \frac{1}{2} m |\mathbf{u}_i|^2 + \frac{1}{2} \sum_{j \neq i} v(r_{ij}) \right] \exp(-i\mathbf{q} \cdot \mathbf{r}_i), \quad (8)$$

where  $u_i$  is the velocity of the  $i$ th particle,  $v(r_{ij})$  is the interaction potential, and  $q$  is taken along the  $z$  axis. For  $q=0$ , we can write

$$J_0^{ez} = \sum_{i=1}^N u_{iz} \left[ \frac{1}{2} m |\mathbf{u}_i|^2 + \frac{1}{2} \sum_{j \neq i} v(r_{ij}) \right] - \frac{1}{2} \sum_{i \neq j} \mathbf{u}_i \cdot \mathbf{r}_{ij} \frac{\partial v(r_{ij})}{\partial z_{ij}}. \quad (9)$$

The Green-Kubo expression for thermal conductivity [9] can be written as

$$\lambda = \frac{1}{Vk_B T^2} \int_0^{\infty} \langle J_0^{ez}(t) J_0^{ez}(0) \rangle dt. \quad (10)$$

It is important to note here that in this expression only interaction among atoms occurs.  $\lambda$  can also be obtained [8] from the knowledge of  $S(q, \omega)$  through the following relation:

$$\frac{n^2 k_B T^2 V \alpha^2}{\lambda} = \frac{1}{2} \lim_{\omega \rightarrow 0} \lim_{q \rightarrow 0} q^2 S(q, \omega), \quad (11)$$

where  $\alpha$  is the thermal-expansion coefficient.

Equations (5)–(7) result in the derivation of the expression [9] of the hydrodynamic structure factor  $S(q, \omega)$  given as

$$S(\mathbf{q} \rightarrow 0, \omega) = \frac{S(\mathbf{q})}{\pi} \left[ \frac{\gamma - 1}{\gamma} \frac{D_T q^2}{\omega^2 + (D_T q^2)^2} + \frac{1}{2\gamma} \left( \frac{\Gamma q^2}{(\omega - cq)^2 + (\Gamma q^2)^2} + \frac{\Gamma q^2}{(\omega + cq)^2 + (\Gamma q^2)^2} \right) \right]. \quad (12)$$

Since we are looking for  $S(q, \omega)$  of the atomic density-density correlation function, the  $\lambda$  involved in the hydrodynamic equation (12) therefore may be due to the contribution of atom-atom interaction only. Electrons may participate indirectly through the interaction potential among atoms. The atomic contribution to  $\lambda$  is known only for liquid Na [10]. This provides the value of thermal diffusivity  $D_T (= \lambda / nC_p)$  equal to  $83.56 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . On the other hand, if we include the electronic contribution to  $\lambda$  [11], the value of  $D_T$  comes out to be  $66.77 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ , which is about three orders of magnitude more than that obtained by including only the atomic contribution. The value of  $D_T$  for Ar [11] is  $80.77 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Thus, we see that the value of  $D_T$  for Na is quite close to that of Ar if we include only atomic contribution. The expression (11) relating  $\lambda$  and  $S(q, \omega)$  has also been used [12] to predict the value of  $\lambda$  and it is found that this expression predicts the value of  $\lambda$  which is very close to atomic contribution in the case of liquid Na. This has also been confirmed by Heyes and March [13].

To understand the extent to which the quasielastic peak could be explained through thermal relaxation, we have plotted the contribution of the first term of hydrodynamic expression (12) by using only an atomic contribution to  $\lambda$ . This is shown in Fig. 1 for two values of  $q$  for liquid Na represented by a solid line. We have also calculated the first term of Eq. (12) by including the electronic contribution to  $\lambda$ ; the results obtained are shown in the inset as a dotted line. From Fig. 1 it can be noted that the contribution due to thermal relaxation is almost negligible if we use the value of thermal conductivity calculated by including the electronic contribution. On the other hand, if  $D_T$  is evaluated using only the atomic contribution to  $\lambda$ , it is found that the quasielastic peak is well taken care of by thermal relaxation. Therefore, it appears that the hydrodynamic model [Eq. (12)] can be applied to conducting liquids if only the *atomic* transport coefficients are considered. Recently, Ishikawa *et al.* [14] studied collective dynamics in dense Hg vapor by performing inelastic x-ray scattering (IXS) experiment. IXS spectra obtained were modeled as a sum of Lorentzians in the framework of generalized hydrodynamics. They, in principle, also made thermal contribution responsible for the quasielastic peak.

Regarding the width of the quasielastic peak, it is found that  $D_T(q)$  in our case does not vary as  $q^{-2}$ . Rather, it may be noted from Fig. 4 of Ref. [1] that going from  $q=1 \text{ nm}^{-1}$  to  $14 \text{ nm}^{-1}$  it falls only 12 times, which seems to be consistent with the observations made for other liquids. Regarding the temperature dependence of the width which SR claims to be

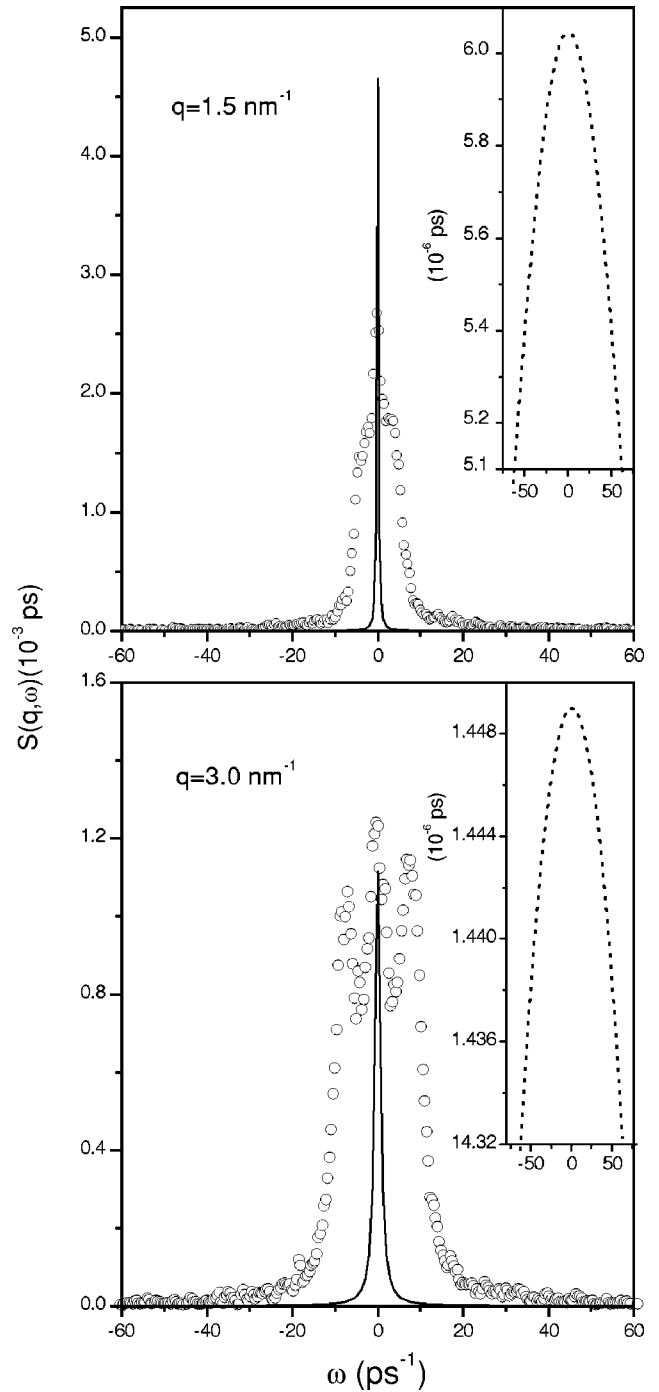


FIG. 1. Open circles represent the dynamical structure factor calculated from x-ray scattering data for liquid Na at 390 K for  $q = 1.5$  and  $3.0 \text{ nm}^{-1}$ . Solid line represents the contribution of the first term of Eq. (12) by using only an atomic contribution to  $\lambda$ . The contribution of the first term by including the electronic contribution to  $\lambda$  is shown in the inset by a dotted line.

strongly temperature-dependent, we attempt below to relate it to the atomic contribution to  $\lambda$ . Electronic contribution to thermal conductivity can be obtained from the famous Wiedemann-Franz law [9] given as

$$\lambda_e = \sigma_{el}TL, \quad (13)$$

where  $L$  is the Lorentz number and  $\sigma_{el}$  is electrical conductivity. For metals,  $\sigma_{el}$  decreases with temperature, thus reducing  $\lambda_e$  as weakly dependent on temperature. On the other hand, an atomic contribution to thermal conductivity is temperature-dependent. Therefore, it appears that a heat diffusion term of some kind definitely enters the processes which are responsible for the quasielastic peak.

One of the issues which arise due to the contrasting memory-function (MF) approach with the standard hydrodynamic model is the appearance of slow relaxation time  $\tau_\alpha$ . The second-order MF which the commenting authors have used in their original work [2–6] can be written as a sum of two or more terms representing binary and multiparticle/collective contributions. The multiparticle effect may have some relation with so-called  $\tau_\alpha$ , which may be calculated through mode-coupling calculations. However, a model MF with single relaxation time [15], which includes the effect of multiparticle correlation to some extent, can qualitatively explain the behavior of the quasielastic peak and Brillouin peaks if the parameters of MF are determined microscopically. The slow  $\alpha$  relaxation can then improve only in quantitative agreement.

Another issue is the interpretation of parameter “ $a$ .” In our work, only  $q \rightarrow 0$  results obtained from the hydrodynamic formula are compared with this parameter. However, our formula Eq. (3) of Ref. [1] in the  $q \rightarrow 0$  limit does not provide parameter “ $a$ ” exactly related to  $\gamma$ . Nevertheless, it describes the ratio of the strength of elastic to inelastic scattering. Thus, the comparison made in Fig. 1 by the commenting authors can only provide guidance for further improvement.

Here, we would also like to point out that all “atomic” transport coefficients are related to each other through the Stokes-Einstein [9] relation (relating the self-diffusion coefficient and shear viscosity) and the relation (relating the self-diffusion coefficient and thermal conductivity) given by Tankeshwar [12]. However, as far as the quasielastic peak is concerned, it can now be said that heat diffusion terms definitely enter the process. However, it remains to investigate whether atomic or electronic contributions or both play a role in studying the dynamical structure factor which provides complete information about *atomic* motions at different length and time scales. Nevertheless, our model provides a useful scheme for studying the line shape of IXS or neutron-scattering spectra.

In the end, we compliment the commenting authors for bringing out these issues, which still require further study.

- 
- [1] Shaminder Singh and K. Tankeshwar, Phys. Rev. E **63**, 012201 (2003).  
 [2] T. Scopigno, U. Balucani, G. Ruocco, and F. Sette, J. Phys.: Condens. Matter **12**, 8009 (2000).  
 [3] T. Scopigno, U. Balucani, G. Ruocco, and F. Sette, Phys. Rev. Lett. **85**, 4076 (2000).  
 [4] T. Scopigno, U. Balucani, G. Ruocco, and F. Sette, Phys. Rev. E **63**, 011210 (2001).  
 [5] T. Scopigno, U. Balucani, G. Ruocco, and F. Sette, Phys. Rev. E **65**, 031205 (2002).  
 [6] T. Scopigno, A. Filipponi, M. Krisch, G. Monaco, G. Ruocco, and F. Sette, Phys. Rev. Lett. **89**, 255506 (2002).  
 [7] T. Scopigno, G. Ruocco, F. Sette, and G. Vilianni, Phys. Rev. E **66**, 031205 (2002).  
 [8] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw Hill, New York, 1980).  
 [9] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1986).  
 [10] M. Shimoji, *Liquid Metals* (Academic Press, London, 1977).  
 [11] P. A. Egelstaff, *An Introduction to the Liquid State* (Clarendon Press, Oxford, 1994).  
 [12] K. Tankeshwar, Phys. Chem. Liq. **24**, 91 (1991).  
 [13] D. M. Heyes and N. H. March, Int. J. Thermophys. **20**, 267 (1999).  
 [14] D. Ishikawa, M. Inui, K. Matsuda, K. Tamura, A. Q. R. Baron, S. Tsutsui, Y. Tanaka, and T. Ishikawa, J. Phys.: Condens. Matter **16**, L45 (2004).  
 [15] K. Tankeshwar, G. S. Dubey, and K. N. Pathak, J. Phys. C **21**, L811 (1988).