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Generalized negative bulk viscosity in liquids

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Abstract. Expressions for the wave number dependent shear viscosity and longitudinal viscosity are obtained using generalized hydrodynamics and Mori formalism. The results obtained for shear viscosity and longitudinal viscosity have been used to calculate the wave number dependent bulk viscosity for the Lennard-Jones potential near its triple point. It has been found that the bulk viscosity becomes negative for wave numbers greater than 0.8 \AA^{-1} .

1. Introduction

The crossover between the hydrodynamics over viscoelastic to free particle regime of the fluid can be studied either through the Boltzmann equation by including correlated collisions or by generalizing the hydrodynamics concept. The generalization of the conventional hydrodynamics involves the introduction of wave vector k frequency ω dependent transport coefficients, implying that the stress tensor and heat current are non-local functions of the gradient of the flow field and temperature. Thus, the generalized transport coefficients introduce a length and time scale into the hydrodynamics and are essentially useful in filling the gap between the hydrodynamics theory and theory applicable in the kinetic regime. The k dependent transport coefficients have been evaluated for the hard-sphere system [1] and very recently in the lattice gas system by Das and co-workers [2] using the kinetic theory approach. One of the important developments of the work of Das *et al*, which we wish to address in this paper, is the existence of the so-called generalized negative bulk viscosity. In fact, the misinterpreted simulation results [3, 4] for negative bulk viscosity in the lattice gas system are accounted for by them as the pure effect of generalized hydrodynamics. For the realistic interaction potential, there exist few studies in the literature for the wave number dependence of shear, longitudinal and bulk viscosities. The zero-frequency wave number dependence of shear viscosity, $\eta_s(k)$, has been studied for the Lennard-Jones (LJ) [5] and Rb [6] liquids by the computer simulation technique. The k dependence of longitudinal viscosity, $\eta_l(k)$, and shear viscosity of liquid Pb have been investigated by Larsson *et al* [7] through experimental study of the dynamical structure factor, $S(k, \omega)$, and simulation study of the transverse current correlation function. The wave vector dependence of the bulk viscosity $\eta_B(k)$ was determined from the relation $\eta_B(k) = \eta_l(k) - 4\eta_s(k)/3$. It was found by Larsson *et al* that the bulk viscosity becomes negative for values $k > 1.2 \text{ \AA}^{-1}$ before it finally approaches zero for very large values of k , but at present there exists no explicit theoretical study for the calculation of the wave vector dependence of the three viscosities, especially of interest in view of the present development of the negative bulk viscosity. Therefore, in the present work, using the concept of generalizing the conventional hydrodynamics, we investigate the existence of negative bulk viscosity for a continuous interaction potential such as the LJ potential.

The layout of the paper will be as follows. In section 2 we derive expressions for the wave number dependent longitudinal and shear viscosity using Mori formalism. Results and discussions are given in section 3. In section 4 we present the conclusion.

2. Expressions for wave vector dependent longitudinal and shear viscosity

We introduce the wave vector and frequency dependent longitudinal viscosity $\eta_1(k, \omega)$ through the following equation [8]:

$$\frac{\partial}{\partial t} J_1(k, t) = -\frac{k^2}{S(k)} \frac{k_B T}{m} \int_0^t dt' J_1(k, t') - \frac{k^2}{nm} \int_0^t dt' \Phi(k, t-t') J_1(k, t') \quad (1)$$

where $J_1(k, t)$ is the longitudinal current-current correlation function and $S(k)$ is the static structure factor. n , m , T and k_B are the number density, mass, temperature and Boltzmann constant. $J_1(k, t)$ is related to the dynamical structure factor by

$$S(k, \omega) = (k^2/\omega^2) J_1(k, \omega). \quad (2)$$

$J_1(k, \omega)$ is the Fourier-Laplace transform of $J_1(k, t)$. The dynamical structure factor is related to the density-density correlation function, $F(k, t)$, by

$$S(k, \omega) = (2/\beta) F''(k, \omega); \quad \beta = (k_B T)^{-1} \quad (3)$$

with $F''(k, \omega)$ as the imaginary part of the Fourier-Laplace transform of $F(k, t)$.

The long-wavelength limit Green-Kubo expression for the longitudinal viscosity is given as

$$\eta_1(0) = \frac{4}{3} \eta_s + \eta_B = (m^2/2k_B T V) \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (\omega^4/k^4) S(k, \omega). \quad (4)$$

From the above equations one finds that $\Phi''(k, \omega)$ could be regarded as the wave vector and frequency dependent longitudinal viscosity i.e. $\eta_1(k, \omega)$. We also find that in order to calculate $\Phi''(k, \omega)$ we need to calculate $J_1(k, \omega)$ or $S(k, \omega)$. For the calculation of $S(k, \omega)$ we use the Mori continued fraction representation [9] given by

$$F(k, \omega) = -\beta S(k)/[\omega + \tilde{M}_n(k, \omega)] \quad (5a)$$

$$M_n(k, \omega) = -\delta_n^1/[\omega + \tilde{M}_{n+1}(k, \omega)]. \quad (5b)$$

In order to calculate $S(k, \omega)$ and hence $\eta_1(k, \omega)$ from the above expressions it is necessary to truncate the hierarchy of equation (5) at a suitable stage. Higher-order relaxation kernels $M_n(k, \omega)$ are mathematically complicated objects due to the restricted time evolution of the fluctuating forces appearing in their expressions. Therefore, one normally restricts the discussion to the second- or third-stage relaxation kernel. Since the exact calculations of these relaxation kernels is not yet feasible, in general, simple approximations for the relaxation kernel can be made, which preserve a number of the important properties of the space-time autocorrelation functions, irrespective of the choice of the relaxation kernel. This approach has been extensively discussed by Boon and Yip [8]. Therefore, in the present work we restrict ourselves to $M_3(k, \omega)$ and assume it to be of the form

$$M_3(k, t) = M_3(k, 0) Q_1(t/\tau_1(q)) = \delta_3^1(k) Q_1(t/\tau_1(q)) \quad (6)$$

where $Q_1(x)$ is even and a decaying function of time. The value of $\tau_1(q)$ is such that the eighth sum rule of $S(q, \omega)$ is exactly reproduced. Taking the $\omega \rightarrow 0$ limit and exploiting equations (1)–(4) we obtain an expression for $\eta_1(k, \omega = 0)$ given by

$$\eta_1(k, 0) = \eta_1(k) = C_1(nm/k^2)[\delta_2^1(k)/\delta_3^1(k)]\tau_1^{-1}(k) \tag{7}$$

where $C_1 = \int_0^\infty Q_1(x) dx$ and $\tau_1^{-2}(k) = \delta_4^1(k)$. The $\delta_n^1(k)$ are called Mori coefficients and are related to the sum rules of the density autocorrelation function up to $2n$ th order. The explicit expressions for a few of them, which are used in the present work, are given by [10]

$$\delta_2^1(k) = \omega_1^2(k) - k^2 k_B T / mS(k) \tag{8}$$

$$\delta_3^1(k) = [C_4^1(k) - (\omega_1^2(k))^2] / \delta_2^1(k) \tag{9}$$

$$\delta_4^1(k) = [C_6^1(k) - \delta_3^1(k) - \omega_1^2(k)((\omega_1^2(k))^2 + 2\delta_2^1(k)\delta_3^1(k))] / \delta_2^1(k)\delta_3^1(k) \tag{10}$$

where $\omega_1^2(k)$, $C_4^1(k)$ and $C_6^1(k)$ are the second, fourth and sixth frequency sum rules of the longitudinal current–current correlation function, respectively. The expressions for fourth and sixth frequency sum rules are given by Bansal and Pathak [11].

Similarly, we introduce the wave vector and frequency dependent shear viscosity through the transverse current–current correlation function $J_t(k, t)$. In the Fourier–Laplace space we have

$$J_t(k, \omega) = -J_t(k, 0) / [\omega + k^2 \bar{K}_1(k, \omega) / nm]. \tag{11}$$

Recalling the Green–Kubo expression, i.e.

$$(m/2k_B T) \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (\omega/k)^2 J_t(k, \omega) = \eta_s / mn \tag{12}$$

we find that in the long-wavelength and zero-frequency limit the $\bar{K}_1(k, \omega)$, i.e. the memory function of the transverse current correlation function, becomes the ordinary viscosity. Therefore $\bar{K}_1(k, \omega)$ is regarded as the k and ω dependent shear viscosity i.e. $\eta_s(k, \omega)$. We follow the Mori continued fraction representation, as described above, to evaluate $\bar{K}_1(k, \omega)$ from the above equations and approximate $\bar{K}_2(k, \omega)$ i.e. the higher-order memory function as

$$K_2(k, t) = K_2(k, 0) Q_2(t/\tau_1(k)) \tag{13}$$

to obtain

$$\eta_s(k) = C_2(nm/k^2)[\delta_1^t(k)/\delta_2^t(k)]\tau_1^{-1}(k) \tag{14}$$

where $\tau_1^{-2}(k) = \delta_5^t(k)$ and $C_2 = \int_0^\infty Q_2(x) dx$. The $\delta_n^t(k)$ are related to the sum rules of the $J_t(k, t)$ up to $2n$ th order. In view of our earlier work [12] on the transport coefficients we derive equations (7) and (14) by going up to the stage of the memory function so as to incorporate the sum rules of the stress tensors up to fourth order in the $k \rightarrow 0$ limit.

3. Results and discussion

In order to calculate $\eta_l(k)$ and $\eta_s(k)$ from expressions (7) and (14) we require the knowledge of the sum rules up to sixth order of $J_1(k, t)$ and of $J_t(k, t)$. The results for these have been taken from the work by Bansal and Pathak. These sum rules involve the pair potential and static pair, triplet and quadruplet correlation functions. For the triplet and quadruplet correlation functions a low-order decoupling approximation has been used. Regarding the validity of the superposition approximation, it has been demonstrated by Bansal and Bruns [13] that the errors involved in the calculation of the sum rules due to the superposition approximation are not of much significance for any k value in contrast to what is generally expected. This conclusion was drawn by performing a computer simulation experiment for the evaluation of the triplet contribution to the fourth sum rule of the longitudinal and transverse current correlation functions at the triple point of argon and comparing the results with those obtained using the superposition approximation. The same conclusion also emerges from the work of Pathak *et al* [14], who performed similar calculations at different densities and temperatures for LJ fluids. Therefore, in the present work we restrict ourselves to the use of the superposition approximation and expect that the results obtained are independent of the approximation used here to estimate the multiparticle contribution to the sum rule.

The only unknowns in the expressions (7) and (14) for the evaluation of wave vector dependent viscosities are now C_1 and C_2 . C_1 and C_2 are numeric constants; e.g., $C_1 = C_2 = (\pi/2)^{1/2}$ for the Gaussian form of the relaxation kernels. In the present work we calculate C_1 and C_2 so as to achieve the exact value of $\eta_l (= 4.44$ mpoise) and $\eta_s (= 2.5$ mpoise) at $k = 0$ near the triple point of the LJ fluids so that the hydrodynamic results ($k \rightarrow 0$) are exactly reproduced by the theory. The results obtained for the three normalized ($\eta(k)/\eta(0)$) viscosities obtained for the LJ fluid are plotted in figure 1 against k . From the figure it is seen that $\eta_s(k)$ and $\eta_l(k)$ decay with k . The decay of $\eta_l(k)$ with k is faster than the decay of $\eta_s(k)$, which results in a negative value of the bulk viscosity for $k > 0.8 \text{ \AA}^{-1}$. From figure 1 it is also observed that $\eta_s(k)$ decays smoothly whereas there is some structure present in the decay of $\eta_l(k)$.

In order to search for the reason for the negative bulk viscosity we have plotted in figure 2 the initial values of the functions $\eta_l(k, t = 0) (= \delta_l^t(k)/k^2)$, $\eta_s(k, t = 0) (= \delta_s^t(k)/k^2)$ and $\eta_B(k, t = 0) (= \eta_l(k, t = 0) - 4\eta_s(k, t = 0)/3)$. From figure 2 it is seen that $\eta_B(k, t = 0)$ becomes negative for $k > 1.4 \text{ \AA}^{-1}$ and it is found to oscillate. From figures 1 and 2 one may conclude that the effect of relaxations $\bar{M}_3(k, \omega = 0)$ and $\bar{K}_2(k, \omega = 0)$ is to further speed up the decay of $\eta_l(k)$ and/or to slow down the decay of $\eta_s(k)$ with k so as to make $\eta_B(k)$ negative at a value of k smaller than that at which $\eta_B(k, t = 0)$ is negative. In order to obtain physical insight we note that $\eta_s(k, t = 0)$ and $\eta_l(k, t = 0)$ are related to $G(k)$ and $\frac{4}{3}G(k) + B(k)$: $G(k)$ and $B(k)$ are the wave vector dependent rigidity modulus and bulk modulus. Therefore, figure 2 implies that it is the bulk modulus that becomes negative for $k > 1.4 \text{ \AA}^{-1}$. This information may be useful in problems related to the elastic instability of the system under external disturbances in which elastic moduli vanish. Our study suggest that in such a system the bulk modulus should vanish faster than the rigid modulus.

The negative value of the bulk viscosity observed in the present theoretical calculations is supported by the findings in a lattice gas model of Das *et al* [2], who extended the Boltzmann equation to be valid in the hydrodynamic regime. It has been shown by Das *et al* that negative bulk viscosity arises due to the non-isotropy of the system at finite k . In fact the isotropy of the lattice gas is an idealization and a limiting property valid only for very small values of k . At finite k lattice gases are no longer isotropic and hence the

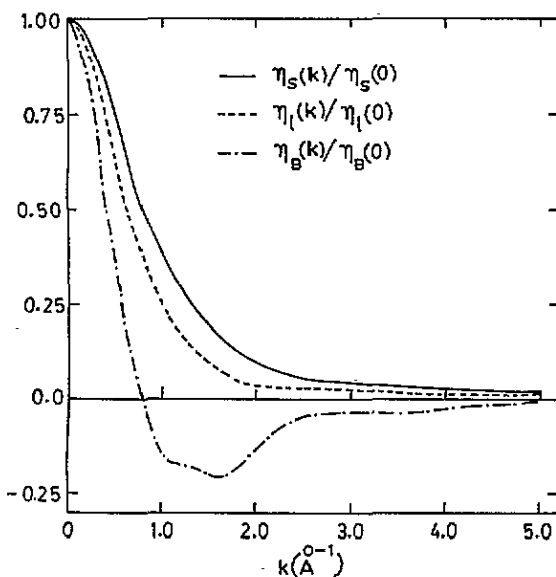


Figure 1. The variation of the three normalized viscosities with wave number k .

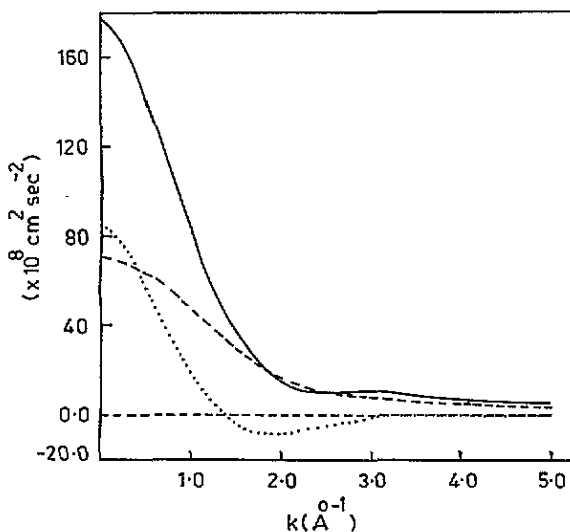


Figure 2. The variation of $\eta_l(k, t = 0)$ (full line), $\eta_s(k, t = 0)$ (dashed line) and $\eta_B(k, t = 0)$ (dotted line) with wave number k .

transport coefficients are direction dependent. With decreasing density the isotropy breaks down at smaller and smaller k values. In fact it has been shown by Das *et al* that the bulk viscosity is negative only for some particular direction of the wave vector k . However, from the present work it is not clear that such a breakdown of isotropy at finite k takes place in our system, which is considered to be an isotropic system. Further, it is not possible either from the nature of the work done here to comment on the physical effects that make the

generalized bulk viscosity negative. Therefore, this remains to be investigated.

4. Conclusion

To conclude, in this paper we have used the concept of generalized hydrodynamics to show theoretically the existence of negative bulk viscosity in LJ fluids. From the present work and the findings of Larsson *et al* [7] for liquid Pb and of Das *et al* [2] for the lattice gas system one expects that the negative bulk viscosity may be a universal phenomenon in liquids and dense fluids. However, this needs more investigation.

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