Modification of a kinetic model of the generalized Enskog equation

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It is pointed out that a previously proposed kinetic model of the generalized Enskog equation does not describe properly the hydrodynamic spectrum of density fluctuations because of the neglect of the momentum state corresponding to the longitudinal stress tensor in the representation of the memory function. It is shown that inclusion of this state leads to a kinetic model which gives results in agreement with light-scattering data.

The kinetic model[1] QTRT (wave-number-dependent triple-relaxation-time model) was originally proposed as a minimal approximation to the generalized Enskog equation[2] satisfying the general constraints of conservation laws, short-time properties, and hydrodynamic behavior. Although it has been used to analyze neutron-scattering measurements on argon[1,3] and neon[4] and computer molecular-dynamics data on Lennard-Jones liquids,[1] the results are not conclusive because of the ambiguity of describing these fluids as a hard-sphere system. The ambiguity does not exist when comparing QTRT calculations with molecular-dynamics data on hard-sphere fluids; in such tests over a wide range of fluid densities it was found that QTRT gives quite accurate time-correlation-function results at wave number $q\sigma \gtrsim 0.5$, where σ is the hard-sphere diameter.[5] However, recently it has been noted that QTRT does not describe correctly the hydrodynamic spectrum of density fluctuations $S(q,\omega)$ as measured by light scattering in xenon,[6] neon,[7] and helium[7] gases.

The purpose of this Comment is to point out that the inadequacy of QTRT in the hydrodynamic regime lies in its neglect of the momentum state of longitudinal stress tensor in the memory-function representation, and to show that a modified kinetic model which includes this state gives agreement with light-scattering data. The absence of the longitudinal-stress-tensor state in QTRT has been recognized by one of us[8] and also by Dufty and Lindenfeld,[9] who showed that significant improvement in the hydrodynamic behavior can be obtained by choosing, as the closure element of the kinetic model or the effective collision frequency, the matrix element of the memory function Σ in the longitudinal-stress-tensor state.

The momentum states used in the QTRT representation of Σ for longitudinal fluctuations are those corresponding to the density, longitudinal momentum, kinetic energy, and kinetic energy current. For the closure element the matrix element of Σ in the state

$$|M\rangle = \frac{1}{\sqrt{30}}\left[\frac{1}{2}\left(\frac{p}{mv_0}\right)^4 - 5\left(\frac{p}{mv_0}\right)^2 + \frac{15}{2}\right],$$

where $v_0^2 = k_B T/m$, has been used[1] mainly because of previous studies of kinetic models of the linearized Boltzmann equation for Maxwell molecules.[10] It can be shown that the QTRT memory function gives for the longitudinal viscosity, $D_l = (\frac{4}{3}\eta + \zeta)/mn$, where η and ζ are the shear and bulk viscosities, respectively, the result[8]

$$(D_l)_{\mathrm{QTRT}} = \frac{\nu\sigma^2}{5} + \frac{v_0^2 5}{2\nu}, \tag{1}$$

where $\nu = 4\sqrt{\pi}\, n\sigma^2 v_0 g(\sigma)$. This is in contrast to the Enskog theory expression, in the first Sonine approximation,[11]

$$D_l = \frac{\nu\sigma^2}{5} + \frac{5v_0^2}{3\nu}(1 + \tfrac{2}{5}y)^2, \tag{2}$$

where $y = \frac{2}{3}\pi n\sigma^3 g(\sigma)$. Since D_l is an important part of the sound-attenuation coefficient, one can understand why QTRT would not give the correct line shape of the Brillouin component in $S(q,\omega)$ in the hydrodynamic regime.

A way to remedy the defect in QTRT is to include the longitudinal-stress-tensor state

$$|\tau\rangle = \frac{\sqrt{3}}{2}\left[\left(\frac{p_z}{mv_0}\right)^2 - \frac{1}{3}\left(\frac{p}{mv_0}\right)^2\right] \tag{3}$$

in the representation of Σ. The additional matrix elements needed to construct the kinetic model equation, using the same notation as Ref. 1, are[8]

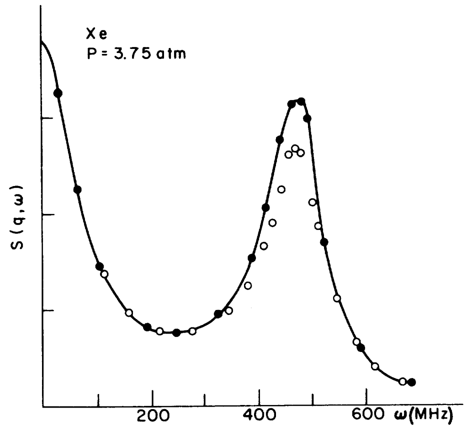

FIG. 1. Dynamic structure factor $S(q,\omega)$ of xenon gas at room temperature and 3.75 atm pressure, and $q\sigma = 8.28 \times 10^{-3}$, for kinetic models QFRT (curve) and QTRT (open circles). Closed circles denote results of linearized hydrodynamics which, when convolved with instrumental resolution, are in essentially perfect agreement with experimental data of 5145-Å incident light scattered at 90° (Refs. 6 and 12). For the kinetic-model calculations $g(\sigma) = 1.013$ and $S(q) = 0.958$.

$$\Sigma(001\,|\,\tau) = qv_0\left(\frac{4}{3}\right)^{1/2} \frac{6y}{5q\sigma}\left[j_1(q\sigma) - \tfrac{3}{2}j_3(q\sigma)\right], \tag{4}$$

$$\Sigma(E\,|\,\tau) = -i\frac{2\sqrt{2\nu}}{3}\, j_2(q\sigma), \tag{5}$$

$$\Sigma(H\,|\,\tau) = qv_0\left(\frac{8}{15}\right)^{1/2} \frac{9y}{5q\sigma}\left[j_1(q\sigma) - \tfrac{3}{2}j_3(q\sigma)\right], \tag{6}$$

$$\Sigma(\tau\,|\,\tau) = -i\tfrac{4}{5}\nu\left[\tfrac{4}{3} - \tfrac{1}{3}j_0(q\sigma) + \tfrac{10}{21}j_2(q\sigma) - \tfrac{6}{7}j_4(q\sigma)\right]. \tag{7}$$

With these matrix elements one has a new kinetic model, which we will denote by QFRT (wave-number-dependent four-relaxation-time model) and which gives Eq. (2) for D_l. One also finds that the modification does not affect the expression for the thermal conductivity.

To examine the hydrodynamic behavior of QFRT we show in Figs. 1 and 2 a comparison of the calculated $S(q,\omega)$ spectra with light-scattering data on xenon gases.[6,12] The hydrodynamic results can be treated as experimental data because, when convolved with instrumental resolution, they are in essentially perfect agreement with the observed spectra. In this comparison the hard-sphere diameter $\sigma = 4.80$ Å was chosen to give the correct value of η, and the other input parameters were $g(\sigma) = (1 - x/2)/(1-x)^3$, where $x = (\pi/6)n\sigma^3$ and $S(q)$ is calculated from the Percus-Yavick approximation.[13]

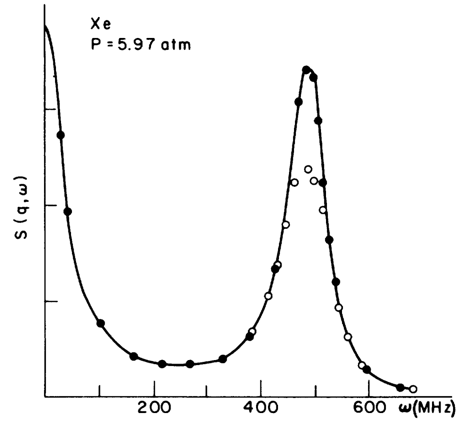

FIG. 2. Same as Fig. 1 except the xenon gas pressure is 5.97 atm, and $g(\sigma) = 1.021$ and $S(q) = 0.935$.

It is seen in Figs. 1 and 2 that QFRT provides an accurate description of density fluctuations in gases at a few atmospheres of pressure. Also seen are the QTRT spectra which show significantly lower intensity for the Brillouin components. The same characteristic deviation was observed in the QTRT comparison with similar data on neon and helium gases.[7]

It is known that light-scattering data on low-density gases in the hydrodynamic or kinetic regime could be very well described by kinetic models of the linearized Boltzmann equation for either hard spheres or Maxwell molecules.[14] It also has been shown by a comparison of kinetic-model calculations for hard-sphere and Lennard-Jones interactions that at low densities $S(q,\omega)$ spectra are insensitive to details of the interatomic potential so long as the collision frequency is chosen to give the same transport coefficient such as η.[15] The kinetic models of the linearized Boltzmann equation cannot adequately describe the experimental data of Figs. 1 and 2 because of nonideality effects not treated by the Boltzmann equation.[6] One may expect from the present results that QFRT should provide a computationally tractable and yet reasonably accurate kinetic theory description of thermal fluctuations in moderately dense gases.

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