Dynamical structure factor of dense gases

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Recent neutron inelastic scattering experiments on dense krypton gases are analyzed using a dynamical theory of simple fluids which includes the correct static susceptibilities but approximates the generalized wave-number- and frequency-dependent transport coefficients by the hard-sphere Enskog-theory values. The full width at half maximum of the dynamical structure factor is found to depend strongly on the thermal pressure coefficient, which is evaluated and discussed for a Lennard-Jones pair potential using the Kirkwood superposition approximation.

In the development of a kinetic theory of dense gases considerable progress has been achieved in obtaining solutions for the thermal fluctuation spectra in the case of hard-sphere fluids and in demonstrating the validity of such calculations by comparison with computer simulation data.[1,2] Also, it was shown[3] that the generalized Enskog theory of a hard-sphere fluid evaluated within the so-called QFRT (wave-number-dependent four-relaxation-time) model[4,5] yields dynamical structure factors in excellent agreement with light-scattering experiments on xenon gas at low and intermediate densities. However, recent neutron inelastic scattering experiments[6] on dense krypton gases revealed significant deviations from hard-sphere results[7] derived from the generalized Enskog equation.

In this Brief Report, we present a first step towards a dynamical theory of dense gases by evaluating the static susceptibilites of the conserved variables using a Lennard-Jones potential while approximating the generalized transport coefficients by their hard-core Enskog values (evaluated within the QFRT model). It is found that in addition to the static structure factor $S(q)$, which for dense krypton gas near the critical density differs markedly from the hard-sphere approximation, especially for $q < q_0$, where q_0 is the position of the first peak in $S(q)$, the wave-number-dependent thermal pressure coefficient also has an important effect on the dynamic structure factor $S(q,\omega)$.

A dynamical theory of a simple fluid may be conveniently expressed in terms of the time correlation functions[8] of the three conserved variables, number density $A_1(\vec{q})$, longitudinal current density $A_2(\vec{q})$, and temperature density $A_3(\vec{q})$,

$$A_1(\vec{q}) = \frac{1}{\sqrt{NS(q)}} \sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{r}_i} , \tag{1a}$$

$$A_2(\vec{q}) = \frac{1}{\sqrt{NmT}} \sum_{i=1}^{N} \vec{p}_i^{\,z} e^{i\vec{q}\cdot\vec{r}_i} , \tag{1b}$$

$$A_3(\vec{q}) = [T\sqrt{C_v(q)}]^{-1}[\,\epsilon(\vec{q}) - A_1(\vec{q}) \times \langle \delta\epsilon^*(\vec{q})\delta A_1(\vec{q})\rangle\,] , \tag{1c}$$

orthogonalized with respect to the thermal average, $\langle \delta A_i^*(\vec{q})\delta A_j(\vec{q})\rangle = \delta_{ij}$, at temperature T (we set $k_B = 1$ throughout this paper). Here

$$\epsilon(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j\neq i} v(r_{ij}) \right) e^{i\vec{q}\cdot\vec{r}_i} \tag{1d}$$

is the energy density, $S(q)$ is the static structure factor, and $C_v(q)$ is the wave-number-dependent specific heat at constant volume. Then the 3×3 matrix equation[9] for the correlation function of these variables is

$$\begin{pmatrix} z & \Omega_{12}(q) & 0 \\ \Omega_{12}(q) & z + q^2 D_l(q,z) & \Omega_{23}(q) + \dfrac{q^3\mu(q,z)}{[n^2 m C_v(q)]^{1/2}} \\ 0 & \Omega_{23}(q) + \dfrac{q^3\mu(q,z)}{[n^2 m C_v(q)]^{1/2}} & z + q^2 \dfrac{\lambda(q,z)}{nC_v(q)} \end{pmatrix} \phi(q,z) = -1 , \tag{2}$$

where $\Omega_{12}(q) = [q v_0/\sqrt{S(q)}]$ and $\Omega_{23}(q) = [q v_0/\sqrt{C_v(q)}]\beta(q)$ are characteristic frequencies of the fluid, $v_0 = \sqrt{T/m}$ is the thermal velocity, and $\beta(q)$ is the wave-number-dependent thermal pressure coefficient. Furthermore, $D_l(q,z)$ and $\lambda(q,z)$ are generalized kinematic longitudinal viscosity and heat conductivity, while $\mu(q,z)$ is a transport coefficient coupling temperature fluctuation and longitudinal current (for further details, see Refs. 4 and 5). The static correlations entering explicitly in the calcu-

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lation of the dynamic structure factor $S(q,\omega) = \pi^{-1}S(q)\,\mathrm{Im}\phi_{11}(q,\omega)$, therefore, are $S(q)$, $C_v(q)$, and $\beta(q)$, which in the long-wavelength limit approach the thermodynamic derivatives[10] $nT\kappa_T$, $(1/n)(\partial e/\partial T)_n$, and $(1/n)(\partial p/\partial T)_n$, respectively, where $\kappa_T = (1/n)(\partial n/\partial p)_T$ is the isothermal compressibility, p is the pressure, and e the energy density. The molecular expression for $C_v(q)$ involves up to four particle correlations and will not be given here,[4] while $\beta(q)$ is given in Eq. (4).

In the present calculation the dynamical properties embodied in the wave-number- and frequency-dependent transport coefficients $D_l(q,z)$, $\lambda(q,z)$, and $\mu(q,z)$ will be approximated by their corresponding hard-sphere expressions, calculated within the generalized Enskog theory (QFRT model) and given in Eq. (36) of Ref. 5. The static correlation functions, on the other hand, will be treated correctly for a fluid with a realistic interaction potential. This means the resulting description will give the correct Landau-Placzek form of $S(q,\omega)$ in the hydrodynamic limit

$$S(q,\omega=0) = \frac{[S(q)]^2}{\pi v_0^2}\left[\mathrm{Im}D_l(q,0) + \frac{n v_0^2[\beta(q) + q^2\mathrm{Re}\mu(q,0)/v_0\sqrt{mn^2}]^2}{q^2\mathrm{Im}\lambda(q,0)}\right] \tag{3}$$

with exact positions of the Brillouin peaks at $\pm c_s q$, c_s being the adiabatic sound velocity. The correct large-q behavior is also assured since the generalized transport coefficients are obtained from a kinetic-equation description.[5]

The theory described above is applied to dense krypton gas at the two thermodynamic states investigated by neutron scattering in Ref. 6: (a) $n_1 = 0.0106$ Å^{-3}, (b) $n_2 = 0.0138$ Å^{-3}, and $T = 297$ K corresponding to $n_1\sigma^3 = 0.482$, $n_2\sigma^3 = 0.628$, $T/\epsilon = 1.47$, using the Lennard-Jones parameters $\sigma = 3.57$ Å; $\epsilon = 201.9$ K of krypton.[11] The hard-core diameter d was chosen as in Ref. 6 to be $d = 3.53$ Å. Furthermore, the experimental structure factor $S(q)$ is used for the characteristic frequency $\Omega_{12}(q)$. We approximated the wave-number-dependent specific heat $C_v(q)$ by its hard-core (and free-particle) value $C_v(q) = \frac{3}{2}$, since we noticed that the full width at half maximum (FWHM) of $S(q,\omega)$ in the intermediate wave-number regime does not depend strongly on $C_v(q)$. This fact becomes plausible from the observation that, on the one hand, does not depend on $C_v(q)$ explicitly and, on the other hand, in the q regime of interest the Lorentzian-like shape of $S(q,\omega)$ is essentially determined by $S(q,\omega=0)$ and its area $S(q)$. In contrast, as is also clear from Eq. (3), $S(q,0)$ is quite sensitive to the thermal pressure coefficient $\beta(q)$. Its explicit expression[4] in terms of the pair potential $v(r)$ and the two- and three-particle correlations is

$$\beta(q) = 1 - I_1(q) - [I_2(q) + I_3(q)]/S(q) \tag{4a}$$

with

$$I_1(q) = \frac{n}{2}\int d^3r\, g(r)\sin(\vec{q}\cdot\vec{r})\frac{\vec{q}\cdot\vec{\nabla}}{q^2}\frac{v(r)}{T}\ , \tag{4b}$$

$$I_2(q) = \frac{n}{2}\int d^3r\, g(r)e^{i\vec{q}\cdot\vec{r}}\frac{v(r)}{T}\ , \tag{4c}$$

$$I_3(q) = \frac{n}{2}\int d^3r\, g(r)e^{i\vec{q}\cdot\vec{r}}\frac{u(r)}{T}\ , \tag{4d}$$

and $u(r)$ is an effective potential

$$u(r) = n\int d^3s\, g(s)v(s)\left[\frac{g_3(\vec{r},\vec{s})}{g(r)g(s)} - 1\right] \tag{4e}$$

which we approximate by using the Kirkwood[12] superposition approximation (KSA). To evaluate the integrals and $S(q)$, entering $\beta(q)$ we use a Lennard-Jones potential and take the pair correlation $g(r)$ from available computer simulations[13] of a L-J fluid for two thermodynamic states with (I) $n\sigma^3 = 0.50$, $T/\epsilon = 1.360$ and (II) $n\sigma^3 = 0.65$, $T/\epsilon = 1.584$, which are closest to the krypton states (a) and (b).

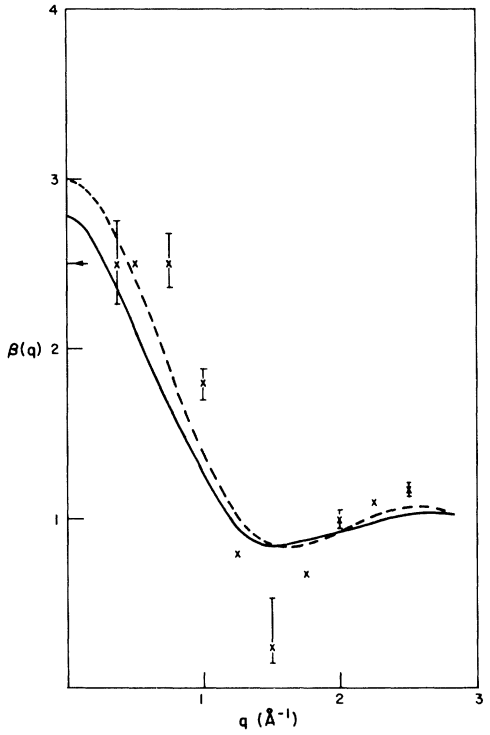

FIG. 1. Wave-number–dependent thermal pressure coefficient $\beta(q)$ for density $n = 0.0106$ Å^{-3}. Full line: present theory; dashed line: hard-sphere result; crosses: fit of $\beta(q)$ adjusted to yield experimental FWHM, error bars being based on the experimental uncertainty, as shown in the data of Ref. 6.

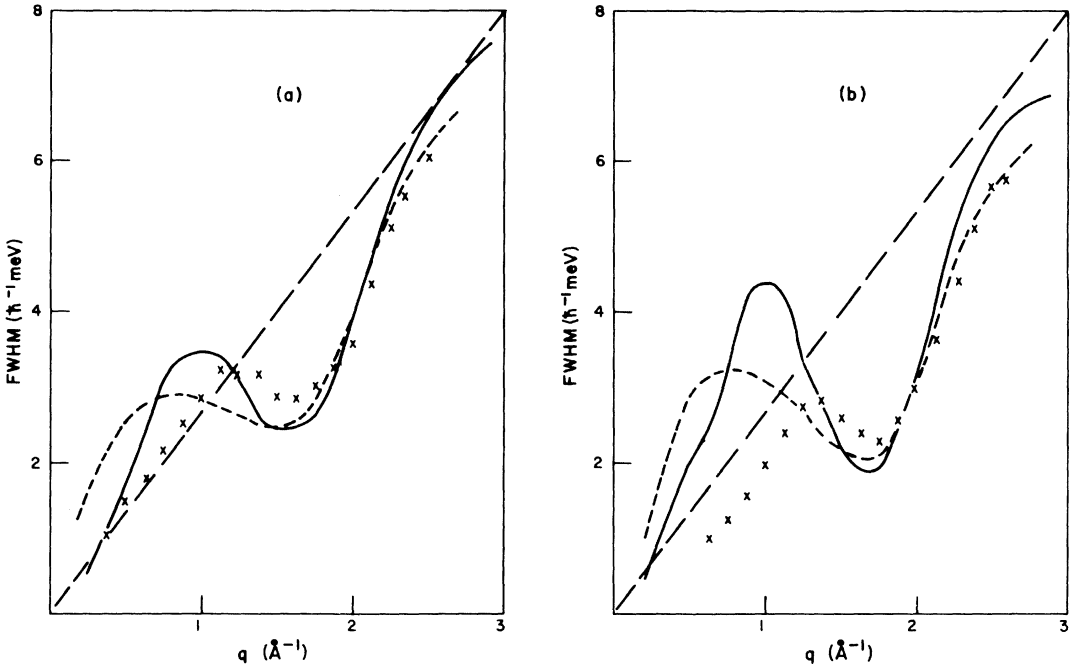

FIG. 2. FWHM of $S(q,\omega)$ for density (a) $n=0.0106$ Å^{-3}; (b) $n=0.0138$ Å^{-3}. Full line: present theory; dashed line: hard-sphere theory (QFRT); straight line: perfect gas; crosses: krypton experiment. All theoretical results have no resolution correction.

The calculated $\beta(q)$ given in Fig. 1 shows considerable wave-number dependence. This is, however, a general feature of dense fluids since the hard-sphere result indicates similar behavior. The FWHM of $S(q,\omega)$ obtained in the present work is compared with the neutron data in Fig. 2. Relative to the hard-sphere results an improvement has been achieved at small q due to the use of the correct $S(q)$. Effects of $\beta(q)$ are quite pronounced at $q\simeq q_0/2$, and agreement in this region is still not satisfactory. If we were to fit the FWHM data by adjusting $\beta(q)$, we would then obtain the results also shown in Fig. 1. It is remarkable that $S(q,\omega=0)$ is then also in good agreement with experiment. Notice that the resonant structure in the fitted curve of $\beta(q)$ is not given by either the hard-sphere theory or the present approximate calculation.

The use of KSA introduces some uncertainty in our calculation of $\beta(q)$. The inadequacy of the KSA for $\beta(q=0)$ has been reported for a dense liquid.[14] An estimate of the possible error involved may be obtained by comparing the approximate $\beta(q=0)$ with values obtained by differentiating Monte Carlo results[15] for the compressibility factor p/nT, indicated by an arrow in Fig. 1. Aside from a direct computer simulation of $\beta(q)$, there appears to be no other way of obtaining more accurate numerical results. Figure 3 shows the evaluated integral $I_3(q)$ and the corresponding results from the fitted $\beta(q)$ assuming the same values of $I_1(q)$ and $I_2(q)$. One sees that the calculation produces the correct qualitative features, particularly the oscillations in $I_3(q)$, in contrast to the comparison in Fig. 1. Thus, strong cancellations occur among the three components of $\beta(q)$ and it is the quantitative difference in Fig. 3 that gives rise to the differences seen in the FWHM. It remains to be determined whether a more accurate evaluation of $\beta(q)$ will give better agreement with the neutron-

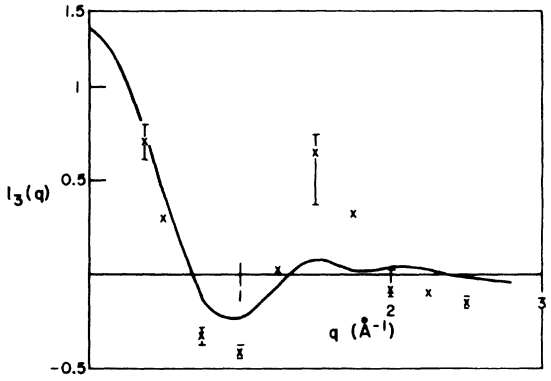

FIG. 3. Three particle contribution $I_3(q)$ to $\beta(q)$ for density $n=0.0106$ Å^{-3}. Full line: present theory using the Kirkwood superposition approximation; crosses: $I_3(q)$ determined from fitted $\beta(q)$ in Fig. 1.

scattering data. One should also keep in mind that the fitted $\beta(q)$ was obtained assuming that the generalized transport coefficients of the dense Lennard-Jones fluid are well approximated by the generalized Enskog theory, which takes into account only uncorrelated binary hard-core collisions.

In conclusion, improved agreement with neutron scattering data of $S(q, \omega)$ compared to a pure hard-sphere theory is obtained, but discrepancies still remain. Although some of the discrepancies may be attributed to the superposition approximation in evaluating $\beta(q)$, it seems clear that further progress will require the treatment of binary collisions dynamics for a realistic pair potential, as indicated by the present analysis of the neutron scattering data.

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