

Experimental Determination of the Linear Term in the Density Expansion of the Dynamic Structure Factor by Means of Neutron Scattering

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The linear term in the density expansion of the dynamic structure factor has been determined experimentally for the first time. We used neutron-scattering data at very low momentum transfer ($0.3 < k < 1.2 \text{ nm}^{-1}$) on room-temperature ^{36}Ar at low density (0.06–0.25 times the critical). Only for $k < 0.95 \text{ nm}^{-1}$, the experimental data agree qualitatively with a corresponding hard-spheres system. We conclude that the linear term is a very sensitive probe for studying the two-particle interaction potential in dilute gases.

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The density-expansion approach is a very useful tool for studying static properties of dilute gases. In many cases it has been applied to the equation of state in order to determine static properties connected to pairs and triplets in molecular systems, such as the second virial coefficient, which provides information on the pair interaction potential. Another application was made recently in neutron-diffraction measurements of the static structure factor $S(k)$ in low-density krypton [1] and argon [2] gases as a function of the density, which allowed the determination of the pure pair and triplet contributions to $S(k)$. In this way the pair and triplet interaction potentials could be investigated in a more direct way than through the equation-of-state virial coefficients.

Dynamical properties of isolated pairs and triplets in low-density gases have been studied over the last twenty years with interaction-induced infrared absorption spectroscopy and depolarized interaction-induced light-scattering spectroscopy (DILS) [3].

However, in the examples given above the approaches are limited in the sense that in the case of $S(k)$, i.e., the zeroth-frequency moment of the dynamic structure factor $S(k, \omega)$, we are concerned only with the density expansion at $t=0$ of the Van Hove density correlation function related with $S(k, \omega)$, while in light-absorption and light-scattering experiments one obtains a frequency spectrum, but only in a limited region of k close to 0. Therefore, it would be of great interest to develop the possibility of experimentally studying the density expansion of the dynamic structure factor $S(k, \omega)$ in a wide range of both k and ω and, therefore, of the Van Hove correlation function in a wide range of r and t . It is to be expected that in this way very detailed information on the pair interaction and possibly on triplet interactions can be obtained, since we believe that the microscopic dynamics is more sensitive to the intermolecular forces than the microscopic structure.

A few theoretical papers have dealt with the problem of the density expansion of time-dependent correlation functions, both in classical as well as in quantum-mechanical systems [4–7]. For the case of classical hard spheres, in particular, it is established that within the framework of the revised Enskog theory, time-dependent correlation functions can be density expanded if the density is low enough and within a density-dependent range of k and ω values [8].

For the general case in which one takes into account the correlation between successive collisions, it is now well established from theoretical calculations that dynamical correlation functions cannot be represented as simple power series of the density for all times, because of nonexponential long-time tails. Therefore, the corresponding spectra also cannot, in principle, be expanded near $\omega=0$. This phenomenon also gives rise to the logarithmic terms in the density expansion of transport coefficients [9]. Both the long-time tails of correlation functions and the logarithmic terms in the transport coefficients are evident in molecular-dynamics calculations and kinetic theory [10,11].

In order to avoid such problems in the analysis of the density behavior of experimental data for $S(k, \omega)$, one should restrict oneself to the (k, ω) range where effects due to long-time tails are negligible within the experimental uncertainties. Or, in other words, one must avoid the region in (k, ω) space where collective modes are manifest in the spectrum of density fluctuations and one must fulfill one of the following two requirements:

$$k \gg 1/l \quad (1)$$

or

$$\omega \gg 1/\tau, \quad (2)$$

where l and τ are the mean free path and mean free time, respectively, in a corresponding hard-sphere system. For

example, in DILS, where the momentum transfer $\hbar k$ between the probe and the sample does not fulfill (1), condition (2) must be satisfied. We will show how well our present experimental data meet this requirement.

Kamgar-Parsi, Cohen, and de Schepper [8] show for hard spheres that binary collisions dominate the dynamics at $kl > 3$, which leads to a linear density dependence of $S(k, \omega)$ at low densities. Therefore, we assume that under condition (1) in a real gas the first correction to the zero-density limit of $S(k, \omega)$ is equivalent to taking into account the dynamics of pairs.

When (1) or (2) is fulfilled and for expansion of $S(k)$ as well as $S(k, \omega)$, one can write

$$\frac{S(k, \omega)}{S(k)} = S^{(0)}(k, \omega) + nS^{(1)}(k, \omega) + O(n^2), \quad (3)$$

where $S^{(0)}(k, \omega)$ is the free-gas contribution and equals the dynamic structure factor for noninteracting particles, and the linear term $S^{(1)}(k, \omega)$ represents the contributions due to the interaction and dynamics of pairs. The higher-order terms in (3) are negligible for

$$n\sigma^3 \ll 1, \quad (4)$$

where σ is the size of the particles. Under conditions (1) and (4) $S^{(1)}(k, \omega)$ is given by [8]

$$S^{(1)}(k, \omega) = \frac{1}{\pi} \text{Re} \left\langle \frac{1}{i\omega + i\mathbf{k} \cdot \mathbf{v}} \Lambda_B \frac{1}{i\omega + i\mathbf{k} \cdot \mathbf{v}} \right\rangle, \quad (5)$$

where $\langle \dots \rangle$ denotes the one-particle velocity average, and Λ_B is the Boltzmann collision operator, which is determined exclusively by the two-particle interaction potential [12]. Using Eq. (5), it is in principle possible to calculate $S^{(1)}(k, \omega)$ numerically from an arbitrary two-particle potential, but this is outside the scope of this Letter.

Until now, the explicit calculation of $S^{(1)}(k, \omega)$ has been carried out only for a classical hard-sphere fluid [5,8]. Kamgar-Parsi, Cohen, and de Schepper [8] use an expansion equivalent to (3) at low density ($V_0/V < 0.1$, which is equivalent to $n\sigma^3 < 0.14$, where V_0 is the close-packing volume). They expand $S(k, \omega)$ in powers of $1/kl_0$, where $l_0 = (n\pi\sigma^2\sqrt{2})^{-1}$ is the Boltzmann mean free path:

$$\frac{S(k, \omega)}{S(k)} = \frac{2}{\pi} \frac{l_0}{kl_0} \left[\exp \left[-\frac{4}{\pi} \omega^*{}^2 \right] + \frac{s_{11}^{\beta}(\omega^*)}{kl_0} + O(kl_0)^{-2} \right], \quad (6)$$

where $l_0 = l_0(\pi M/8k_B T)^{1/2}$ is the Boltzmann mean free time, M the particle mass, k_B Boltzmann's constant, and T the temperature. The frequency dependence appears only through the reduced variable $\omega^* = \omega l_0/k l_0$. The first term in Eq. (6) is the free-gas term, while $s_{11}^{\beta}(\omega^*)$ is re-

lated to $S^{(1)}(k, \omega)$ by

$$s_{11}^{\beta}(\omega^*) = \left(\frac{k_B T}{\pi M} \right)^{1/2} \left(\frac{k}{\sigma} \right)^2 S^{(1)}(k, \omega), \quad (7)$$

and is a function of ω^* only. Kamgar-Parsi, Cohen, and de Schepper [8] find that for $kl_0 > 3$ the first two terms in Eq. (6) are sufficient for a correct description of the hard-sphere dynamics. In the present paper we will use this result for comparison with experimental data.

We have measured $S(k, \omega)$ of room-temperature ($T/T_c = 2$) ^{36}Ar at three thermodynamic states, with pressures of 2, 5, and 8 MPa, corresponding to $n = 0.49, 1.23, \text{ and } 2.00 \text{ nm}^{-3}$ or $n\sigma^3 = 0.02, 0.05, \text{ and } 0.08$, respectively (using $\sigma = 0.34 \text{ nm}$ for argon), which fulfills condition (4) as well as $V_0/V < 0.1$. The large coherent scattering cross section of ^{36}Ar (77.9 b) enabled us to obtain a good scattering signal even at the lowest density. The measurements have been carried out with the time-of-flight spectrometer IN5 at the Institut Laue-Langevin (ILL), Grenoble, modified in order to reach a k range much lower than in conventional neutron-scattering experiments [13,14].

In the present data the wave-vector transfer at elastic scattering is in the range $0.3 \leq k \leq 1.2 \text{ nm}^{-1}$, corresponding to $1.2 \leq kl_0 \leq 4.7$ at the lowest density $n = 0.49 \text{ nm}^{-3}$, to $0.5 \leq kl_0 \leq 1.9$ at $n = 1.23 \text{ nm}^{-3}$, and to $0.3 \leq kl_0 \leq 1.2$ at $n = 2.00 \text{ nm}^{-3}$. Consequently, a good deal of the data near $\omega = 0$ do not fulfill condition (1) or (2). This implies that in particular at $n = 1.23$ and 2.00 nm^{-3} at the smaller k and ω values in the density expansion of $S(k, \omega)$, a logarithmic term $n^2 \ln n$ may have some effect and that the linear term may contain contributions from three-particle dynamics [9,11].

The data analysis consists of two parts. The first is the extraction of the fully corrected $S(k, \omega)$ at all densities [15,16], and the second part is the determination of the two-body contribution $S^{(1)}(k, \omega)$. A very accurate normalization was impossible to achieve, probably due to some differences between the geometries of the argon and the vanadium samples, resulting in an estimated systematic error of about 15%. This, however, does not affect the comparison with the theory, since we compare the experimental $S(k, \omega)$ divided by the experimental normalization (calculated as described in Ref. [15]) with the theoretical prediction for $S(k, \omega)/S(k)$. Because the data vary rather smoothly with k , we averaged the experimental data over k intervals of 0.1 nm^{-1} in order to improve the statistics.

First, we obtained $S^{(1)}(k, \omega)$ using the 2-MPa data only, by inverting Eq. (3),

$$S^{(1)}(k, \omega) = \frac{1}{n} \left[\frac{S(k, \omega)}{S(k)} - S^{(0)}(k, \omega) \right], \quad (8)$$

using the well-known free-gas Gaussian for $S^{(0)}(k, \omega)$ given by the first term in Eq. (6). We note that $S^{(1)}(k, \omega)$ is determined rather inaccurately because the

difference between the two terms in Eq. (8) is typically of the order of only a few percent. This is an intrinsic difficulty in this kind of experiment, which can be partially overcome only by performing very accurate measurements. Moreover, since the deviation from $S^{(0)}(k, \omega)$ decreases with increasing k , useful data can be obtained only at very small k , a condition fulfilled for all k values of our experiment.

Next, using the weighted least-squares method, we fitted, at each (k, ω) point, a straight line as a function of n with zero intercept (i.e., only one parameter) to the experimental data for $S(k, \omega)/S(k) - S^{(0)}(k, \omega)$ at 2 and 5 MPa, and also to the data at 2, 5, and 8 MPa. The resulting mean-square deviation δ^2 (i.e., the sum of squares divided by the number of degrees of freedom) is given in Table I for each value of k averaged over all ω . For $k \geq 1.0 \text{ nm}^{-1}$ the fit to three densities is better or of equal quality as compared to the fit to only the two lower densities. We conclude that for $k \geq 1.0 \text{ nm}^{-1}$ and $n \leq 2.00 \text{ nm}^{-3}$ $S(k, \omega)$ is linear in the density. This conclusion is supported by the observation that the fitted parameter $S^{(1)}(k, \omega)$ is not significantly different for the fits at two or at three densities. Thus, for the determination of the linear term $S^{(1)}(k, \omega)$ at $k \geq 1.0 \text{ nm}^{-1}$ we used the experimental data at 2, 5, and 8 MPa. At $0.5 < k < 1.0 \text{ nm}^{-1}$, δ^2 is larger for the three-density fits (but the difference is not as large as for $k \leq 0.5 \text{ nm}^{-1}$). This must be due to the fact that the data at $k < 1.0 \text{ nm}^{-1}$ and $n = 2.00 \text{ nm}^{-3}$ are not linear in n . Moreover, from the drastic increase of δ^2 at $k \leq 0.5 \text{ nm}^{-1}$ when adding the third density $n = 2.00 \text{ nm}^{-3}$ in the fit, we conclude that higher-order terms are probably already significant for $n < 1.23 \text{ nm}^{-3}$, which is also indicated by the fact that at $k \leq 0.5 \text{ nm}^{-1}$, $S^{(1)}(k, \omega)$ obtained from only the lowest density differs considerably from the result of the fits to the two lower densities. In other words, the region of linear behavior in n expands with k , similarly as for light-scattering data, where the region of linear

TABLE I. Mean-square deviation δ^2 for the least-squares fit of $S^{(1)}(k, \omega)$ with two and three densities, respectively. For each k the numbers are averaged over all ω .

$k \text{ (nm}^{-1}\text{)}$	δ^2	
	Two densities	Three densities
0.3	1.13	3.18
0.4	0.36	2.57
0.5	0.48	3.21
0.6	0.73	1.39
0.7	0.88	1.57
0.8	1.14	1.52
0.9	0.87	1.13
1.0	1.01	1.02
1.1	0.99	0.84
1.2	0.93	0.72
Average	0.89	1.40

behavior in n expands with ω (see, e.g., Ref. [3]). Therefore, for the determination of $S^{(1)}(k, \omega)$ at $0.5 < k < 1.0 \text{ nm}^{-1}$, we used the fit to the data at $n = 0.49$ and 1.23 nm^{-3} , and at $k \leq 0.5 \text{ nm}^{-1}$ we used only the data at the lowest density, in the way described in the previous paragraph. We conclude that we obtained the true linear term $S^{(1)}(k, \omega)$ in the density expansion of $S(k, \omega)$, with the possible exception of the region $k \leq 0.5 \text{ nm}^{-1}$; we cannot check the linear density dependence of $S(k, \omega)$ for $n \leq 0.49 \text{ nm}^{-3}$ with the help of data at lower density.

In Fig. 1 we plot the hard-sphere theoretical $s_{11}^B(\omega^*)$ taken from Ref. [8] for various k values and as a function of the reduced frequency ω^* , together with the corresponding quantity for argon obtained from the experimental $S^{(1)}(k, \omega)$. Note that $s_{11}^B(\omega^*)$ should be indepen-

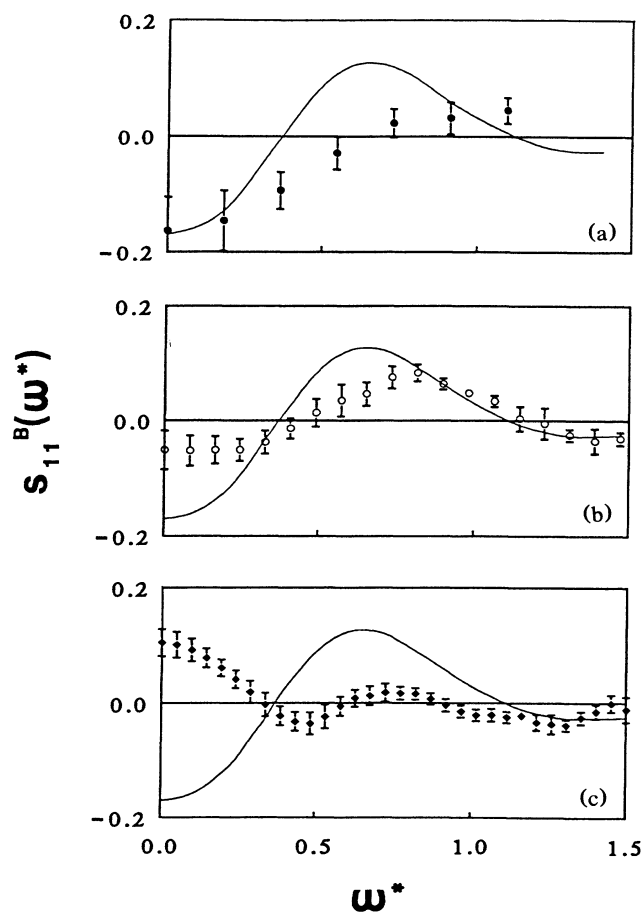


FIG. 1. $s_{11}^B(\omega^*)$ for argon at room temperature (symbols with error bars) and for hard spheres according to Kamgar-Parsi, Cohen, and de Schepper [8] (solid line). Experimental data are from (a) $k = 0.3 \text{ nm}^{-1}$ and $n = 0.49 \text{ nm}^{-3}$; (b) $k = 0.7 \text{ nm}^{-1}$, $n = 0.49$ and 1.23 nm^{-3} ; (c) $k = 1.2 \text{ nm}^{-1}$, $n = 0.49$, 1.23 , and 2.00 nm^{-3} . Note that the experimental points are correlated due to interpolation in the data-reduction procedure; the error bars are estimated from the propagation of the standard deviation of the statistical errors in the measurements.

dent of k , which is apparently not the case for the experimental data. There is qualitative agreement for $k < 0.7 \text{ nm}^{-1}$, but at larger k , quantitative discrepancies are clearly visible, especially at the lower frequencies ($\omega^* < 0.4$). Since kl_0 is close to 1 for part of the data leading to the results in Fig. 1, this might be due to three-particle contributions in $S^{(1)}(k, \omega)$ (see Refs. [9] and [11]), or even to interference from a logarithmic term. However, from Kamgar-Parsi and Sengers [11], it can be seen that for the transport coefficients of hard spheres at densities corresponding to those of the present experiment the first term following the linear one, viz. $n^2 \ln n$, is at least 1 order of magnitude smaller than the linear term. Therefore, we conclude that the differences in Fig. 1 between the experimental data and the hard-sphere results are due first to the difference between the argon potential and hard spheres, which at these low densities cannot account at all for the pair interaction in real systems, and second, at lower ω , possibly to contributions from three-particle events in the linear term.

In conclusion, we have shown for the first time that inelastic neutron scattering at low angles can be performed in low-density gases and analyzed in terms of density expansions in order to obtain information on the two-body dynamical properties in a way similar to what has been done for the static properties. It should be stressed that this was only possible through the availability of the inelastic low- k neutron-scattering facility at the time-of-flight spectrometer IN5 of ILL. We have found that, within the experimental uncertainties, a linear density dependence of the deviation from the free-gas $S(k, \omega)$ exists for $0.5 < k < 1.0 \text{ nm}^{-1}$ at densities $n \leq 1.23 \text{ nm}^{-3}$ and for $1.0 \leq k \leq 1.2 \text{ nm}^{-1}$ even at $n \leq 2.00 \text{ nm}^{-3}$, which, however, cannot be described in terms of hard-sphere dynamics. Also, we have shown that the dynamics in argon at room temperature and low density does not scale with kl_0 , as would be the case for a hard-sphere system. Thus, we have demonstrated that the linear term is very sensitive to the shape of the two-particle potential and that in principle we have a new experimental technique to obtain information on the two-particle potential. Explicit calculation of the linear term with a realistic potential, based on a general theory [17], can in principle be performed and would be desirable for fruitful comparison

with the experiments.

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